

### Remarks Section

The new claims 1-45 submitted with this amended application replace the claims of the original specification of 3/14/2000 (old claims 1-45). Original claims 1-45 of 3/14/2000 are cancelled. The new claims have been placed in proper dependent and independent form. Claims 1,4, and 41 are independent claims and the rest of them are dependent claims. The new claims comply with the Examiner's Office Summary Action of 1/29/2002, pages 6-15, and rectify the claim objections and claim rejections under 35 USC-#112 and 35 USC-#103, as was pointed out by the Examiner. The new claims refer to the elected invented processes.

The two inventors of this application are joint inventors in all 45 new claims submitted with this substitute specification.

The substitute specification contains no new matter, is double spaced and is divided into 67 paragraphs.

An updated listing of previous references in the Information Disclosure Statement is also provided including the patents listed in last form PTO-892 by the Examiner.

### Rebuttal to Claim Rejections under 35 USC-#103

The claim rejection under 35 USC-#103 is requested to be traversed based on the following remarks (referring to both the new and original specifications):

The processes described within this application are utilizing permreactor designs that are substantially different than the one presented in Itoh's and Oertel's paper. This makes the described processes new and capable to be patented. Specific details on the benefits, novelties of the processes, and differences from previous processes are described in pages 5,6,7 of the section Background of the Invention.

In summary, the installation and operation of the second membrane to withdraw hydrogen out the first annular zone is novel. This is because no other process until now in

patent literature teaches similarly consecutive hydrogen separation and continuous reaction-enhancement operation by a second membrane, for the reactions described, which makes the use of the second membrane not obvious, taking into account the many process and reactor variations which have been described in the literature. The purpose of separating hydrogen out of the second membrane is not merely for separation or purification as pointed out in page 14 of the Office response. Hydrogen separation with installation and use of the second membrane has the purpose of driving continuously the catalytic reactions occurring within the first membrane. Thus, the real purpose of using the second membrane is to lower the partial pressure of the separated hydrogen in the annular space between the two membranes. If hydrogen is not removed continuously by the use of the second membrane, the partial pressure of hydrogen will build up along the membrane length in the annular space, and at some point of the reactor the hydrogen will backpermeate into the first catalytic zone. This effect is detrimental for the operation of the membrane reactor/permreactor and the reactions in the first zone will stop due to the presence of hydrogen product. Withdrawal of hydrogen by the second membrane allows for continuous equilibrium shift and for higher conversions and yields in the first catalytic membrane zone for the occurring reactions, which makes the use of the consecutive second membrane to be novel in the described reaction process operations. The use of the two membrane process makes a new process which operates independently for each reaction occurring, is compact in operation, more economic because it eliminates additional off-gas purification process steps, and specific in purpose to power fuel cells and to feed distinct synthesis reactors. These distinctions are not obvious to the person having ordinary skill in the art to which the said subject matter pertains;

Moreover, the process described in the invention, uses a first membrane which is permeable to other chemical components as well and not only to hydrogen, while the Itoh's and Oertel's processes both are using hydrogen only permeable metal-type membranes. Thus, the use of ceramic or composite materials in first membrane cylinder is a significant process difference by the two previous articles. These materials are

projected to be more economic (les expensive) than the metals (e.g., palladium, palladium-silver) that are almost exclusively used for metal membranes.

Similarly, novelty is presented also in the modified process in which the second membrane separates both hydrogen and carbon dioxide out of the annular zone and the binary mixture is used in special fuel cell and synthesis reaction applications. Continuous separation of both components out of the annular zone allows for the reaction to proceed beneficially in the first catalytic zone and offer increased conversions and yields. Lack of permeation of these two gases from the second membrane will yield to a terminal stopping of the reactions in the first catalytic zone due to the backpermeation of hydrogen and carbon dioxide into this zone. This detail is not obvious to a person having ordinary skill in the art to which said subject matter pertains.

Moreover, the internal specification of the presented process permreactors are distinct in comparison with the ones presented by Itoh and Oertel. This stands for the heating elements and the way of heating the described permreactors and related processes. Also it stands for the developed (gradually reduced) pressure gradient from the inner to the outer membrane and the related zones. Also it stands for the unique way the gas mixture is fed, separated, and directed in consecutive applications in the different sections of the permreactor process, as shown in detail in Figure 2 of the drawings.

Another distinct difference of the described processes is their specific use in interconnected fuel cells and synthesis reactors. The specific delivery of gas mixtures rich in hydrogen and carbon oxides in specific types of fuel cells is distinct. Distinct are also the synthesis reactions which consume the generated hydrogen mixtures from the described processes as was pointed out in the Office Summary. Distinct are also the combination of processes utilizing the permreaction operation and the consecutive separation processes (both membrane permeation and cryogenic separation) which are also related and continue the previous USpatent #6,090,312. These distinctions are not obvious to the person having ordinary skill in the art to which said subject matter

pertains; and these distinctions make the described processes patentable over the previous art.

In summary the described processes with the limitations set are new and differ substantially from previous art. Based on the new (rewritten) claims of the current substitute specification and based on the above remarks/comments, the applicants request from the Office to allow this patent application with the accompanied claims.

The processes described here are of significant interest for developmental purposes in the described technology areas/sectors in both national and international level. The applicants have been invited to present this work at national and international technical conferences. The acceptance of the patent by USPO is going to protect the rights of this invention which occurred in USA.

Part of the processes described here is intended to be published also in consecutive publications in order to increase the possibility of their commercial use and to show their innovative usages in fuel cells and synthesis reactions.



**Amendment by substitute specification**

**Application number: #09/525,176**

**Filing Date: 03/14/2000**

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**“Version with markings to show changes made”  
(with respect to the original specification,  
3/14/2000)**

Deleted Matter is shown in brackets, e.g., [membrane reactor]

Added matter is shown in bold letters e.g., **permreactor and separator**,

## **TITLE OF THE INVENTION**

[ PERMREACTOR AND SEPARATOR TYPE FUEL PROCESSORS FOR  
PRODUCTION OF HYDROGEN AND HYDROGEN, CARBON OXIDES  
MIXTURES]

**PROCESSES COMBINING MULTIWALL PERMREACTORS AND  
SEPARATORS FOR FUEL CELLS AND SYNTHESIS APPLICATIONS**

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### **[ References Cited**

#### **U.S. PATENT DOCUMENTS**

4,713,234	12/1987	Weirich et al.
4,810,485	3/1989	Marianowski et al.
5,229,102	7/1993	Minet et al.
5,637,259	6/1997	Galuszka et al.
5,639,431	6/1997	Shirasaki et al.

5,658,681	8/1997	Sato et al.
5,861,137	1/1999	Edlund et al.
5,938,800	8/1999	Verrill et al.

#### OTHER REFERENCES

- Alternative generation of  $H_2$ , CO and  $H_2$ ,  $CO_2$  mixtures from steam-carbon dioxide reforming of methane and the water gas shift with permeable (membrane) reactors, S. Vasileiadis et al., Chem. Eng. Comm., Vol. 176, pp.247-252, (1999).
- Environmentally benign hydrocarbon processing via single and integrated permreactors, permeators, S. Vasileiadis et al., in Reaction Engineering for Pollution Prevention, Elsevier Science Eds. (2000).
- Reactor-Membrane permeator cascade for enhanced recovery and production of  $H_2$  and  $CO_2$  from the catalytic methane steam reforming reaction, Z. Ziaka et al., Chem. Eng. Comm., Vol. 156, 161, (1997).
- Novel reactor-membrane permeator methane-steam reforming process for enhanced recovery of  $H_2$  and  $CO_2$ , Z. Ziaka et. al., 5th World Congress in Chemical Engineering, Symposium Series, San Diego, CA July (1996).
- N. Itoh et al., "Development of a novel oxidative palladium membrane reactor", AIChE Symp. Ser., No. 268, Vol. 85, 10 (1989).
- R. Zhao et al., "Studies on palladium membrane reactor for dehydrogenation reaction", Sep. Sci. & Tech., 25(13-15), 1473 (1990).
- M. Oertel et al., Chem. Eng. Technol., 10, 248 (1987).

-Introductory permreactor, permeator hydrocarbon, carbon oxide processors for externally reformed-(gas phase) fuel cell systems, S. Vasileiadis and Zoe Ziaka, submitted for publication, Aug. 1999.

-Polymer membrane reactors for enhanced hydrocarbon conversion and upgrading, S. Vasileiadis and Zoe Ziaka, Invention Disclosure Document #414880, marked 3/6/1997. ]

#### **CROSS REFERENCE TO RELATED APPLICATIONS**

Continuation in part of Ser. No. 08/595,040, now U.S. Patent 6,090,312 (Jul. 2000)

#### **STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT**

Not Applicable

#### **REFERENCE TO A "SEQUENCE LISTING," A TABLE, OR A COMPUTER PROGRAM LISTING APPENDIX SUBMITTED ON COMPACT DISC**

Not Applicable

#### **[TECHNICAL FIELD]**

This invention relates to new process and reactor designs including permeable reactors (permreactors) and permeators for the hydrocarbon steam reforming, hydrocarbon carbon dioxide reforming, combined hydrocarbon steam and carbon dioxide reforming, alcohol steam reforming, water gas shift, paraffin dehydrogenation, methanol synthesis, and combination of these conversion reactions for production of valuable fuels and chemicals. It also relates to the utilization of the end reaction products such as pure hydrogen, hydrogen and carbon monoxide, hydrogen and carbon dioxide, and mixtures of



these species, into specific applications such as fuel cells, gas turbines, gas engines and synthesis reactors. ]

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

[This current application is continuation in part of the application # 08/595040 filed 1/31/1996.]

[ This current invention describes new and improved process and reactor designs which involve permeable reactors (permreactors) and permeators for the hydrocarbon steam reforming, hydrocarbon carbon dioxide reforming, combined hydrocarbon steam and carbon dioxide reforming, alcohol steam reforming, the water gas shift reaction, dehydrogenation reactions of hydrocarbons, such as dehydrogenation of alkanes (i.e., paraffins) to alkenes, and combination of these previous reactions.

The reactions and heats of reactions that are referred to and utilized within the embodiments of the invention are well known and are listed below: ]

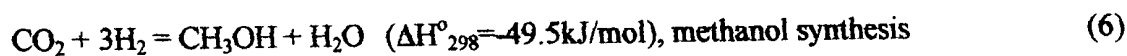
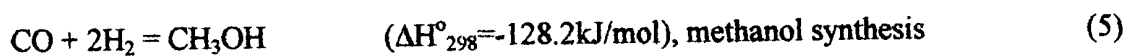
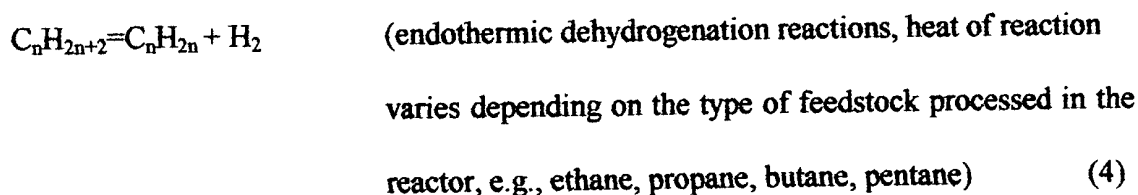
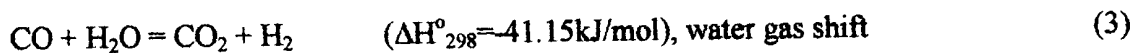
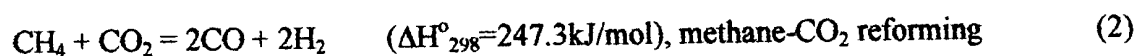
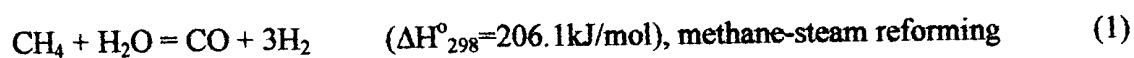
1. This invention relates to new process designs referring to double wall or multiwall type permeable reactors (so called double wall permreactors or double wall membrane reactors) and to consecutive separators, including membrane type and cryogenic separators, for conducting mainly the hydrocarbon steam reforming, hydrocarbon carbon dioxide reforming, combined hydrocarbon steam and carbon dioxide reforming, alcohol steam reforming, water gas shift, paraffin dehydrogenation, methanol synthesis, and combination of these carbon based fuel conversion reactions for the production of valuable upgraded fuels and chemicals. The invention also relates to the utilization of the end reaction products such as pure

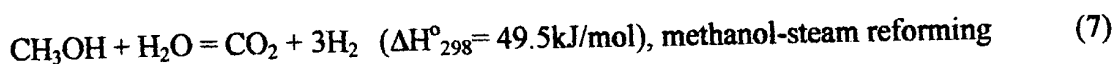
hydrogen and synthesis gas (hydrogen and carbon monoxide, hydrogen and carbon dioxide mixtures), and mixtures of these, into specific applications of consecutive fuel cells, gas turbines, gas engines and synthesis reactors by application of uniquely presented process configurations.

2. Description of the Related Art including Information disclosed under 37 cfr 1.97 and 1.98

2 The current invention describes new and improved processes which involve double wall or multitube permeable reactors (multitube permreactors or membrane reactors) and downstream separators for the hydrocarbon-steam reforming, hydrocarbon-carbon dioxide reforming, combined hydrocarbon steam and carbon dioxide reforming, alcohol steam reforming, the water gas shift reaction, dehydrogenation reactions of alkanes (paraffins), and combination of these previous reactions.

3 The reactions and heats of reactions that are referred to and utilized within the embodiments of the invention are well known and are listed below:





4 [These are catalytic reactions utilizing catalysts such as nickel (Ni), ruthenium (Ru), rhodium (Rh), palladium (Pd), platinum (Pt), chromium (Cr), copper (Cu), zinc (Zn), Cobalt (Co), Gold (Au) and other metals, and bimetallic catalyst compositions of these metals. The catalysts are supported on alumina ( $\text{Al}_2\text{O}_3$ ), titania ( $\text{TiO}_2$ ), silica ( $\text{SiO}_2$ ), zirconia ( $\text{ZrO}_2$ ), lanthanum ( $\text{La}_2\text{O}_3$ ) and other supports, enriched with earth metals such as Ca, La, Na, K.]

4 **The aforementioned are catalytic reactions utilizing active metals as catalysts in monometallic, bimetallic, or multimetallic metal compositions. The catalysts are supported on inorganic oxides such as on various types of alumina and enriched with earth metal additives to enhance catalytic activity and feedstock conversion and minimize deposition of carbon on active metal sites and loss of activity.**

5 Use of [reactor and membrane permeator configurations] **related processes involving catalytic reactor with downstream permeator configurations and systems of those were disclosed in our previous US patent [application: # 08/595040,] #6,090,312 (July 2000). Use of these reactor-separator systems increase the overall process efficacy by increasing the total conversion of [the following] feedstocks such as the following: natural gas, landfill gas, coal gas, hydrocarbons, hydrocarbons- $\text{CO}_2$  mixtures, methane, methane- $\text{CO}_2$  mixtures, alcohols. Moreover, the yields to hydrogen and carbon monoxide or hydrogen and carbon dioxide are increased by the use of the integrated membrane type permeators which [separates] separate effectively the  $\text{H}_2$  and  $\text{CO}_2$  [gases] gas constituents out of the reformed streams. Process efficiency is further improved by the recycling of unreacted and non-separated (non-permeated) hydrocarbon**

(e.g., methane) and carbon monoxide into the first (primary) reactor (reformer) or the alternative direction of the same stream into a consecutive catalytic reactor (reformer or water gas shift reactor) for additional production of hydrogen and carbon dioxide. Direct utilization of the produced and separated hydrogen, synthesis gas, and hydrogen-carbon dioxide mixtures from these processes into consecutive synthesis reactors, fuel cells and gas turbines and engines are additional advantages and {continual} continuing applications and utilizations of the proposed processes.

6 [Current invention elaborates on the substitution of the primary conventional reactor (i.e., reformer, water gas shift, dehydrogenation reactor) by a permeable (membrane-type) reactor (so called permreactor for simplicity) of specific design, and the correspondingly derived improved process and permeable reactor-separator configurations for the above mentioned reactions. Moreover, introduction and specification of double wall permreactors, besides the single wall permreactors, for conducting similar reactions are also disclosed. The described permreactors are designed to consist of interconnected parts which can be readily taken apart and assembled when service is necessary. For the disclosed integrated reaction-separation systems specific applications are disclosed such as the utilization of the end products and/or permeated (separated) streams into consecutively placed synthesis reactors (including additional reformers or water gas shift reactors), gas turbines and engines, and various types of hydrogen based fuel cells and related fuel cell systems.]

6 Current invention elaborates on the introduction and specification of double and multiwall type membrane reactor processes (double and multiwall permreactor

processes) related to the above reactions which can be implemented accordingly, as described below.

7 A specific problem in parallel gas separation and reaction within microporous membrane reactors (permreactors) is the lack of selective separation for the target compound (e.g., hydrogen) in certain materials. Thus, microporous inorganics and composites materials allow the permeation through the membrane of not only the targeted compound but also of other reaction products and reactants that compete for permeation based on their molecular diameter or molecular weight. This effect, separates in the permeate of the membrane reactor a stream which is not pure but needs further separation in order to be utilized as a pure compound (e.g., hydrogen gas for synthesis or fuel). Therefore, capital and operation costs are increased when a single wall membrane reactor process of the above structure is to be used. The introduced double and multiwall permreactor process solves this problem by applying a second consecutive membrane which only separates the targeted compound. For hydrogen separation as an example, a second metal or metal alloy membrane can be used, placed after the first microporous membrane, as described below.

8 The described permreactors wherein the processes are occurring, are designed to consist of interconnected parts which can be readily taken apart, cleaned, serviced and assembled when service or maintenance is necessary. For the disclosed integrated reaction-separation systems specific applications are disclosed such as the utilization of the end products and/or of the permeated (separated) streams into consecutively placed synthesis reactors (including additional reforming

or water gas shift reactors), gas turbines and engines, and various types of hydrogen and methanol driven fuel cells.

9 [Previous reactor and permeable reactor designs from the above cited references refer mainly to methane and methanol steam reforming reactions but not to carbon dioxide reforming, water gas shift and dehydrogenation reactions as the present invention does. Moreover, previous inventions refer to a single reactor or permreactor or other reaction vessel instead of reactor-separator systems as the present invention describes. Present invention introduces double permeable-wall (double membrane-wall) reactors for hydrocarbon and alcohol processing reactions. The double membrane-wall reactors can be of various designs as disclosed within the embodiments of the invention. These can be catalytic reactors as adapted to specific process requirements in terms of setting key operating variables such as reaction temperature, pressure, space velocity, feed composition, to deliver final products (i.e., hydrogen and synthesis gas) in the purity and throughput required by consecutive applications. Moreover, flexibility in the selection of permreactor wall materials such as metals, inorganics, organics and composites, allows design of multifunctional permeable reactors which separate and deliver specific species (e.g., gases) with the required purity and throughput to consecutive applications. Flexibility in the selection of functional and specific permreactor wall materials for each process operation have also economic advantages. Current disclosed permreactor, separator, and overall process designs can utilize membrane materials selected from classes of metals, inorganics (non-porous or porous), polymers, carbons and carbonaceous materials, and composites. Therefore, the selection of less expensive

membrane materials for a specific permreactor, permeator and process operation is available with current invented designs.]

9 Previous reactor and permeable reactor (membrane reactor) designs from the above cited references refer mainly to methane and methanol steam reforming reactions but not to carbon dioxide reforming, water gas shift and dehydrogenation reactions as the present invention also does. Moreover, previous inventions refer to processes occurring within a single reactor or permreactor or other reaction vessel instead of reactor-separator systems as the present invention describes. Present invention introduces processes which are based on double wall and multiwall permreactors for conducting conversion-upgrading reactions of primary and secondary hydrocarbon and alcohol mixtures.

The double wall membrane reactors can be of various designs and be made by various appropriate materials as disclosed within the embodiments and claims of the invention. The catalytic reactors are adapted to specific process requirements in terms of setting values of key operating variables such as reaction temperature, pressure, space velocity, feed composition, catalyst composition and weight, in order to deliver final products (such as hydrogen and synthesis gas) in the required purity and throughput for the consecutive applications. Selection of such variables like temperature, pressure, and feed composition in the different compartments of the described membrane reactor system is also of significant importance. This is because an interconnection and synergetic activity between the various compartments occurs during operation with reaction and separation operations to occur at the same time. Moreover, flexibility in the selection of the double wall permreactor materials such

as metals, inorganics, polymers, and composites, allows for the design of processes which separate and deliver specific species (such as specific gases) with the required purity and throughput to the consecutive applications. Flexibility in the selection of functional and specific permreactor wall materials for each process operation have also economic advantages. Therefore, the selection of less expensive membrane materials and manufacturing techniques for a specific permreactor, permeator and overall process is available with the current invented designs and will affect (reduce) the cost of the overall process operation.

10 Present invention also teaches the direct utilization of end product streams to consecutive synthesis reactors, fuel cells, gas turbines and gas engines. Use of such low pollution energy systems with increased efficiency is of updated interest in utility, energy, chemical, refinery, automobile and environmental companies. Present invention focuses on converting and upgrading primary hydrocarbon feedstocks such as methane, natural gas, coal gas, refinery feedstocks such as naphtha, [and] alcohol feedstocks such as methanol, [and] ethanol and higher alcohols into [to] higher calorific value hydrogen and carbon oxide mixtures[.]. Also [also] it focuses on converting secondary, flue, and waste hydrocarbon feedstocks such as acidic natural gas, biomass gas, flue gas rich in  $\text{CO}_2$  and  $\text{CH}_4$  to same valuable end products. Therefore, present invention describes also environmentally benign [reactor designs and process designs] processes which abate and upgrade at the same time, among the other feedstocks, otherwise waste gases to valuable hydrogen, synthesis gas, and hydrogen-[and] carbon dioxide mixtures. The [In] in situ conversion of carbon dioxide containing hydrocarbon mixtures to alternative fuels and chemicals including hydrogen, and the subsequent



mitigation [abatement] of the carbon dioxide negative atmospheric and terrestrial greenhouse effects [can be] are considered [an] additional benefits from the implementation of [the] this invention.

## **BRIEF SUMMARY OF THE INVENTION**

### **[ SUMMARY OF THE INVENTION ]**

11 [ The present invention discloses double wall permeable reactors and the related elaborate reactor designs, which offer operational advantages by conducting in-situ reactions, in comparison with single wall permeable reactors and conventional non-permeable reactors. Consequently, three different permeable reactor configurations are disclosed. These reactor designs are applied to catalytic hydrocarbon and alcohol reforming, water gas shift and hydrocarbon dehydrogenation reactions. The first design is a double wall permreactor which consists of three concentric hollow cylindrical tubes with the two inner ones to be made by permeable metal, inorganic, carbon or polymer materials depending on the type of feedstocks used and the desired composition of final exit streams. Heating tubes run through the most-inner cylinder which is also filled with the main reaction catalyst. Similarly, the second reactor design consists also of three concentric hollow cylindrical tubes with the two inner ones to be made by permeable metal, inorganic, carbon or polymer materials but with the main reaction catalyst to be contained in the annular space between the most-outer and the next-inner tubes. Heating in this design is achieved by heating the external side of the most-outer tube. Third reactor design consists of an outer impermeable tube which nests multiple organic polymer or composite polymer tubes for gas permeation. Outer tube contains also the

main reaction catalyst which is located around the polymer tubes. Heating is achieved by external heating of the outer tube. ]

11 The present invention discloses processes which consist of double wall or multiwall permreactors and systems of such advanced reactors with consecutively placed separators and reactors to perform specific process operations. These integrated chemical-mechanical systems offer operational advantages by conducting in-situ reactions, in comparison with single wall permeable reactors and conventional impermeable reactors. Consequently, different double wall permreactor processes are disclosed. These are used in catalytic hydrocarbon and alcohol reforming, water gas shift, hydrocarbon dehydrogenation reactions. The first process comprises of a double wall permreactor which incorporates three concentric hollow cylindrical tubes with the two inner ones to be made by permeable (and permselective) inorganic, composite or metal materials depending on the type of feedstocks used, the reactions and reaction conditions occurring, and the desired composition of the final exit streams. Heating tubes run through the most-inner cylinder which is also filled with the main catalyst to conduct the appropriate reaction. Additional catalyst can be placed in the two outer annular spaces created between far outer and next inner and between next inner and most inner tubes. By varying the catalyst position and catalyst type this process can be applied to a number of different reactions. Similarly, the second process involves a double wall permreactor which consists of three concentric hollow cylindrical tubes with the two inner ones to be made by permeable (and permselective) inorganic, composite or

metal materials and with the catalyst for the main reaction to be contained in the annular space between the far outer and the next inner cylindrical tubes. Heating in this process is applied into the external side of the far outer tube. By applying catalyst at the different annular spaces created between the concentric tubes, this process can be applied to various reactions. The two processes differ in the heat and mass transfer profiles and distribution across the radial and axial distances. Use of the described advanced permreactor processes offer significant increases in conversion of reactants and increases in yield and selectivity of products. This is achieved via improved mass and heat transfer, and improved reaction rates within the defined reaction and catalyst zones of the process as described above. Also, the effect of removing products out of the defined reaction zones during the reaction, increases the reactant conversion and the yield to useful products by shifting the equilibrium of the occurring reactions to the product side. Further, use of the described permreactors allows for systems of reactions to take place and be combined in the same module. Synergetic effects of utilizing products and/or reactants of these reactions to conduct improved processes in a consecutive and/or parallel manner is also a result of this invention.

12 [Moreover, the invention pertains to systems of the described permeable reactors with consecutive permeators for separation and further processing of post-reaction gases exiting from the reactors. Permeators can be made by polymer membranes for the concomitant separation of hydrogen and carbon dioxide gases or by metal, non-porous inorganic and carbon membranes for the separation of hydrogen only. These

permreactor-permeator systems are applied to combined hydrocarbon steam and carbon dioxide reforming, hydrocarbon steam reforming, hydrocarbon carbon dioxide reforming, alcohol steam reforming, water gas shift and paraffin dehydrogenation reactions for increasing the reactant conversion and the yield to hydrogen, carbon monoxide and carbon dioxide. The separated hydrogen and carbon oxides are used in further chemical synthesis reactions and as fuel in fuel cells, gas turbines and gas engines. The invention also includes hydrocarbon-CO<sub>2</sub>-steam reforming systems of permreactors with cryogenic separators wherein the consecutive permeators are replaced by cryogenic separators and pure hydrogen and carbon monoxide are recovered as final products. Similar permreactors are also directly interconnected with solid oxide fuel cells for use of the products hydrogen, carbon monoxide and steam as direct fuel in the anode of the cell. Finally, the invention includes use of the disclosed permreactors in series with methanol synthesis and methanol reforming reactors for final production of methanol, hydrogen and carbon dioxide for use as synthesis chemicals or fuels. Detailed description of the invention are presented in the embodiments of the following Figures.]

**12** Moreover, this invention pertains to combined processes of the described permreactors with consecutive permeators and reactors for further separation and processing of the post-reaction gases exiting from the permreactors. Permeators can be made by polymer, composite or metal membranes for the downstream concomitant separation of hydrogen and carbon dioxide gases, or for the separation of hydrogen only. These permreactor-permeator systems are applied to combined hydrocarbon steam and carbon dioxide reforming, hydrocarbon-steam reforming,

hydrocarbon-carbon dioxide reforming, alcohol steam reforming, water gas shift, paraffin dehydrogenation. The processes are capable to increase the reactant conversion and the yield to hydrogen, carbon monoxide, and carbon dioxide. The separated hydrogen and carbon oxides can be used in consecutive chemical synthesis reactions and as fuel in fuel cells, gas turbines and gas engines.

13 The invention also includes hydrocarbon-carbon dioxide-steam reforming process which consists of permreactors with cryogenic separators wherein the consecutive cryogenic separators replace the permeators, and a pure mixture of hydrogen and carbon monoxide is recovered as a final product. Similar permreactors as described above are directly interconnected with solid oxide and molten carbonate fuel cells for using the product hydrogen, carbon monoxide and the unreacted steam as direct fuel in the anode of the cell. Further, the invention includes use of the disclosed permreactors in series with methanol and hydrocarbon synthesis reactors for final production of methanol and hydrocarbons and use as fuels or synthesis chemicals.

#### [ BRIEF DESCRIPTION OF THE DRAWINGS]

14 [ Fig.1, shows the cross section of a concentric double permeable wall cylindrical reactor with tubular type heaters located along the catalyst zone, consisting of an inner metal, non-porous or porous inorganic, or carbon membrane tube and an outer membrane tube made by metal, non-porous inorganic, carbon or organic membrane enclosed within a far-outer impermeable tube.

Fig.2, shows multiple double permeable wall reactors of those described in Fig.1, but without the external impermeable tube, which are placed symmetrically inside a larger common stainless steel tube, to create a multiple tube reactor with a common external area for collecting final permeate hydrogen.

Fig.3, shows a cross section of a concentric double permeable wall cylindrical reactor, consisting of an outer impermeable tube, a next-inner membrane tube made by metal, non-porous or porous inorganic, or carbon membrane, and a most-inner membrane tube made by metal, non-porous inorganic, carbon or organic membrane.

Fig.4, shows multiple double permeable wall cylindrical reactors of those described in Fig.3, which are placed symmetrically inside a larger stainless steel tube, to create a multiple tube reactor with a common external heating area.

Fig5., shows a cross section of a multiple permeable membrane tube reactor wherein the membranes are made by an organic or composite polymer and are nested within an outer impermeable tube.

Fig.6, shows a system of a catalytic permreactor and a consecutive permeator or optionally a system of two catalytic permreactors in series for hydrocarbon steam and  $\text{CO}_2$  reforming or for hydrocarbon  $\text{CO}_2$  reforming only. The reject from the permeator stream containing non-permeate hydrocarbon and CO can be optionally fed into a consecutive catalytic steam reforming reactor.

Fig.7, shows a similar process as in Fig.6 in which the initial feedstock consists only of CO and steam, to undergo water gas shift reaction only in the first catalytic permreactor. The reject from the permeator, CO stream, can be recycled into the initial permreactor or optionally fed into a consecutive water gas shift reactor.

Fig.8, shows a permreactor-permeator or reactor-permeator system applied for catalytic dehydrogenation of  $C_1$ - $C_4$  or higher alkane hydrocarbons; the reject from the membrane permeator olefinic stream can be used for polyolefin production.

Fig.9, shows a catalytic permreactor-permeator system for the hydrocarbon steam reforming reaction. The reject from the membrane permeator hydrocarbon and CO stream can be recycled into the initial reformer or fed into a consecutive steam reforming reactor.

Fig.10, shows a system of a catalytic permreactor or impermeable reactor with a consecutive cryogenic separator for hydrocarbon steam and  $CO_2$  reforming or for hydrocarbon  $CO_2$  reforming only. The one stream separated from the cryogenic separator, containing hydrocarbon,  $CO_2$  and steam can be alternatively fed into the inlet of the initial reforming reactor.

Fig.11, shows a system of a catalytic permreactor or impermeable reactor for hydrocarbon steam and  $CO_2$  reforming or hydrocarbon  $CO_2$  reforming only with complete conversion of hydrocarbon and  $CO_2$  gases to  $H_2$  and CO, which product mixture is fed directly into a SOFC (solid oxide fuel cell) unit for electric current generation.

Fig.12, shows a system of a catalytic permreactor or impermeable reactor followed by a membrane permeator for hydrocarbon steam and  $CO_2$  reforming or hydrocarbon  $CO_2$  reforming only with complete conversion of hydrocarbon and  $CO_2$  feedstocks to  $H_2$  and CO which product mixture enters into the permeator which separates  $H_2$  via permeation from CO.

Fig.13, shows a system of a catalytic permreactor for hydrocarbon, steam and  $\text{CO}_2$  reforming or hydrocarbon  $\text{CO}_2$  reforming only with a consecutive methanol synthesis reactor from hydrogen, CO and  $\text{CO}_2$  or hydrogen and CO only followed by a methanol steam reforming reactor for production of  $\text{H}_2$  and  $\text{CO}_2$ . The system of reactors includes recycling streams of  $\text{H}_2$  and  $\text{CO}_2$  for increasing the overall process efficacy. }

#### **BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS**

**14a** Fig.1, shows a vertical cross sectional view of a concentric double wall cylindrical process permreactor with tubular type heaters located along the inner main catalyst zone, consisting of an inner membrane tube and an outer membrane tube enclosed within a far outer impermeable tube.

**14b** Fig.2, shows a sectional view of the same process permreactor as in Fig.1, including the three catalyst beds, the two cylinder type inner and outer membrane tubes, the inner axial heating elements, and the inlet and outlet ports in each section of the permreactor.

**14c** Fig.3, shows multiple double wall process permreactors of those described in Fig.1, but without the far outer impermeable tube, which are placed symmetrically inside a larger common impermeable metal tube, to create a multiple tube permreactor with a common external area for collecting final permeate hydrogen.

**14d** Fig.4, shows a cross section of a similar concentric double wall process permreactor, consisting of a far outer and heated impermeable tube, a next inner membrane tube and a most inner membrane tube:



14e Fig.5, shows multiple double wall process permreactors of those described in Fig.4, which are placed symmetrically inside a larger impermeable metal tube, to create a multiple tube permreactor with a common external heating area.

In the Figures below, the permreactors can be any of those described in Fig.1, Fig.3, Fig.4, Fig.5 above.

14f Fig.6, shows a combined process which includes a catalytic permreactor in series with a consecutive permeator or a reactor for hydrocarbon and alcohol steam and CO<sub>2</sub> reforming, hydrocarbon CO<sub>2</sub> reforming only, and water gas shift. The reject from the permeator stream containing non-permeate hydrocarbon and CO can be optionally fed into a consecutive catalytic steam reforming reactor.

14g Fig.7, shows a similar process with this in Fig.6, in which the initial feedstock consists only of carbon monoxide (CO) and steam to undergo only the water gas shift reaction in the first catalytic permreactor. The reject from the permeator, CO stream, can be recycled into the first permreactor or optionally fed into a consecutive water gas shift reactor.

14h Fig.8, shows a permreactor-reactor process applied in the catalytic dehydrogenation of C<sub>1</sub>-C<sub>4</sub> or higher alkane hydrocarbons. The reject stream from the permreactor rich in olefins is fed in the consecutive reactor for production of polyolefins or specialty chemicals.

14i Fig.9, shows a catalytic permreactor-permeator process for the hydrocarbon or alcohol steam reforming reaction. The reject from the membrane permeator hydrocarbon, alcohol, and carbon monoxide stream can be recycled into the initial reformer or fed into a consecutive (second) steam reforming reactor.

14j Fig.10, shows a process of a catalytic permreactor which combines a consecutive cryogenic separator for hydrocarbon steam and CO<sub>2</sub> reforming or for hydrocarbon CO<sub>2</sub> reforming only reactions. The liquified stream separated from the cryogenic separator, containing hydrocarbon, CO<sub>2</sub> and steam can be fed into the inlet of the initial reforming reactor. The gaseous stream from the separator contains H<sub>2</sub> and CO.

14k Fig.11, shows a process which includes a catalytic permreactor for hydrocarbon steam and CO<sub>2</sub> reforming or hydrocarbon CO<sub>2</sub> reforming only with complete conversion of hydrocarbon and CO<sub>2</sub> gases in the reactor to H<sub>2</sub> and CO, which product mixture is fed directly into a SOFC (solid oxide fuel cell) or a MCFC (molten carbonate fuel cell) unit for electricity generation.

14l Fig.12, shows a process which includes a catalytic permreactor for hydrocarbon, steam, and CO<sub>2</sub> reforming or hydrocarbon CO<sub>2</sub> reforming only with a consecutive methanol synthesis reactor from hydrogen, CO and CO<sub>2</sub> or from hydrogen and CO only. Methanol from the second reactor can be used as fuel, synthesis chemical, or as feed in a methanol powered fuel cell for electricity generation.

[ DETAILED DESCRIPTION OF THE DRAWINGS ]

15 [Fig.1 shows a cross section of the membrane reactor to be used in steam and carbon dioxide reforming of hydrocarbons, steam reforming of alcohols, water gas shift and dehydrogenation reactions, which consists of a concentric double wall cylindrical assembly with tubular type heaters located within the catalyst, along the catalyst zone. An outer impermeable tube (7) nests the two permeable concentric tubes. Reacting

feedstocks such as steam and hydrocarbon,  $\text{CO}_2$  and hydrocarbon, steam,  $\text{CO}_2$  and hydrocarbon, steam and alcohols, or alkanes (paraffins) such as ethane, propane, n-butane, i-butane, pentane, naphtha and higher paraffins, are fed within the main catalyst zone (4) through special inlet fittings and they react in the catalyst to produce hydrogen, carbon monoxide, carbon dioxide. Optionally, small volumetric quantities of hydrogen can be added into above feedstocks to prevent heavy catalyst deactivation in the reactor inlet, wherein propensity for hydrocarbon cracking into carbon is high in absence of any hydrogen. The hydrocarbon reforming catalyst can be nickel, ruthenium, rhodium, palladium enriched with earth type metals such as potassium, calcium, magnesium, lanthanum, cerium, and supported on alumina, silica, titania, zirconia or other inorganic oxide. For the water gas shift reaction the catalytic metal can be nickel, also iron, copper, zinc, chromium, cobalt enriched with and supported on similar metal oxides. The methanol reforming catalysts can be zinc, chromium, copper, iron, nickel, ruthenium, rhodium, palladium. Finally, the above described reactor design is applied as well for paraffin (alkane) dehydrogenation reactions and the reactor becomes a catalytic dehydrogenator which utilizes platinum, chromium, palladium catalysts enriched with and supported on similar inorganic oxides.]

#### **DETAILED DESCRIPTION OF THE INVENTION**

15     Fig.1 shows the top cross section of the double wall processing permreactor used in steam and carbon dioxide reforming of hydrocarbons, steam reforming of alcohols, water gas shift and alkane dehydrogenation reactions. It consists of a concentric double membrane wall cylindrical assembly with tubular type heaters located within the catalyst, along the most inner main catalyst zone. A far outer

impermeable tube (7) nests the two permeable concentric tubes (1) and (2). Reacting feedstocks such as steam and hydrocarbons,  $\text{CO}_2$  and hydrocarbons, steam,  $\text{CO}_2$  and hydrocarbons, steam and alcohols, or alkanes such as ethane, propane, n-butane, i-butane, pentane, naphtha and higher paraffins, are fed within the main catalyst zone (4) through special inlet fittings and react in the catalyst to produce hydrogen, carbon monoxide, carbon dioxide or olefins. Optionally, small volumetric quantities of hydrogen can be added into above feedstocks to prevent the deactivation of catalyst in the inlet of the reactor, wherein propensity for hydrocarbon cracking into carbon is high in the absence of hydrogen. The hydrocarbon reforming catalysts can be nickel, ruthenium, rhodium, palladium, chromium, cobalt, enriched with earth type metals such as calcium, lanthanum, potassium, magnesium, cerium, yttrium, and supported on oxides of alumina ( $\text{Al}_2\text{O}_3$ ), titania ( $\text{TiO}_2$ ), silica ( $\text{SiO}_2$ ), zirconia ( $\text{ZrO}_2$ ), lanthanum ( $\text{La}_2\text{O}_3$ ), types of glass or on other inorganic or metal oxides. For the water gas shift reaction the catalytic metals can be nickel, iron, copper, zinc, chromium, cobalt enriched with similar earth metals and supported on similar metal oxides. The methanol reforming catalysts can be zinc, chromium, copper, iron, nickel, cobalt enriched with and supported on similar metal and metal oxides. Finally, the described permreactor process is applied as well for alkane dehydrogenation reactions and it becomes a catalytic dehydrogenation process which utilizes platinum, chromium, palladium, rhodium, ruthenium catalysts enriched with and supported on similar metal and inorganic oxides. The above catalysts are also used in the next embodiments (figures) of the described reaction-catalysis processes.

16 [Hydrogen is removed along the inner membrane tube (2), wherein the membrane is made by a metal or inorganic (non-porous or porous), porous inorganic-metal or carbon material. Carbon monoxide, carbon dioxide, steam, hydrocarbons, alcohols may also permeate through first membrane in a lesser degree than hydrogen if the membrane is porous inorganic or inorganic-metal. An inert carrier gas such as argon, nitrogen, steam or a mixture of these gases may flow along the permeate annulus, between tubes (2) and (1), through suitable inlet fittings, to carry the permeate components at a specific pressure value. Permeate hydrogen is further removed through permeation along the outer membrane tube (1) so that permeated stream contains pure hydrogen only, with pure hydrogen to be used in various applications including feed to synthesis reactors, gas turbines and engines, and fuel cells. Outer membrane tube (1) is made by a metal, non-porous inorganic or carbon membrane which allows only hydrogen to permeate through, and therefore purifies hydrogen from the permeating carbon oxides, steam and hydrocarbons, in the annular zone between the two membrane tubes.]

16 The reactant pressurized gas is fed into the main catalytic zone (4) and the pressure in this zone is maintained the highest. The pressure drops progressively from zone (4) to zone (8) to zone (5), with outer zone (5) to be at the lowest pressure. This pressure gradient is necessary to maintain an outward permeation and flow of the selective gases radially from membrane (2) to membrane (1). Hydrogen is removed first along the most inner membrane tube (2), wherein the membrane material is an inorganic or composite material. Carbon monoxide, carbon dioxide, steam, hydrocarbons, alcohols may also permeate through first membrane (2) in a

lesser degree than hydrogen. An inert carrier gas such as argon, nitrogen, steam or a mixture of these gases may also flow along the permeate annulus, between tubes (2) and (1), through suitable inlet fittings, to carry the permeate components at a fixed pressure. Permeate hydrogen is further removed via permeation along the next inner membrane tube (1), so that permeated stream contains pure hydrogen only, with pure hydrogen to be used in various applications including feed to synthesis reactors, gas turbines and engines, and fuel cells. Next inner membrane tube (1) is made by a metal or non-porous inorganic membrane which allows only hydrogen to permeate through, and therefore purifies hydrogen from the permeating carbon oxides, steam, alcohols and hydrocarbons, flowing in the annular zone between the two membrane tubes.

17 [ Metal materials permeable to hydrogen for the membrane tubes (1) and (2), include palladium, vanadium, and palladium alloys such as palladium-nickel, palladium-silver, palladium-zinc, palladium-chromium, palladium-copper, palladium-tungsten and others. Hydrogen permeable non-porous inorganic membranes include silicon carbide, silicon nitride, tungsten carbide, tungsten nitride, titanium carbide, titanium nitride, tantalum carbide, tantalum nitride and others. Porous inorganic membranes include alumina, silica, titania, zirconia, various types of glass and others. Carbon type membranes are made by deposition or other fabrication method (i.e., pyrolysis) of carbon or carbonaceous materials within a porous substrate to make it hydrogen permeable.

Metal and metal alloys can be deposited on porous inorganic or metal surfaces to make them hydrogen permeable. Palladium and other metal deposition as membranes

can be done with electroless plating, electroplating, sputtering, chemical vapor deposition, physical vapor deposition and other applicable metal deposition or metallization techniques. Inorganic, inorganic-metal membrane materials can be deposited as well in porous inorganic or metal surfaces via various deposition techniques including incipient wetness, dip coating and sol gel methods. ]

17     **Metal materials permeable to hydrogen for next inner membrane tube (1) include palladium, vanadium, palladium alloys such as palladium-nickel, palladium-silver, palladium-copper, palladium-tungsten and others. Hydrogen permeable non-porous inorganic membranes include silicon carbide, silicon nitride, tungsten carbide, tungsten nitride, titanium carbide, titanium nitride, tantalum carbide, tantalum nitride and others. Porous and microporous inorganic membranes for the most inner tube (2) include oxides of alumina, silica, titania, zirconia, various types of glass and others. Composite type membranes for tube (2) are made by deposition or fabrication of a polymer or metal into a porous inorganic substrate (support) to make it hydrogen or hydrogen and carbon dioxide permeable. Inorganic membrane materials are made or modified via various deposition techniques including incipient wetness, dip coating and sol gel methods.**

**Metal and metal alloys for next inner tube (1) are also deposited on porous inorganic or metal surfaces to make them hydrogen permeable. Palladium and other metal deposited membranes are fabricated by electroless plating, electroplating, sputtering, chemical vapor deposition, physical vapor deposition and other applicable metal deposition or metallization techniques.**

18 [ Organic polymer, composite or copolymer membranes can be made by polymers such as polyimides, polycarbonates, polysulfones, polybenzimidazoles, polyphosphazenes, polyamides, polystyrenes, polycaprolactams, parylenes, polyvinyl halides, polyacetates, polysiloxanes and others to be permeable to hydrogen or to hydrogen and carbon dioxide. Finally, composites of the previous materials can be also made as hydrogen permeable membranes such as inorganic-metal, inorganic-organic, inorganic-metal-organic composites. Metal and metal alloy, non-porous inorganic and carbon membranes are highly selective to hydrogen, while porous inorganic, organic, and composite membranes are usually selective to other species as well. The disclosed double permeable wall reactor design can be fabricated by selecting among the aforementioned materials to satisfy process requirements for the reactor itself and the consecutive application processes disclosed later in the text. ]

18 Organic polymer, composite, or copolymer membranes are made by polymers such as polyimides, polycarbonates, polysulfones, polybenzimidazoles, polyphosphazenes, polyamides, polystyrenes, polycaprolactams, parylenes, polyvinyl halides, polyacetates, polysiloxanes and others in order to be permeable to hydrogen or to hydrogen and carbon dioxide. Composites of materials are made as hydrogen or hydrogen and carbon dioxide permeable membranes and are based on inorganic-metal, inorganic-organic, inorganic-metal-organic composites. Metal, metal alloys, non-porous inorganic, membranes are highly selective to hydrogen, while porous and microporous inorganic, polymer, and composite membranes are also selective to other species as well including carbon dioxide. The disclosed double wall permreactor process can utilize among the aforementioned materials to satisfy the



necessary process requirements. The described membranes (1), (2) can also act as catalytic materials to partly catalyze the occurring reactions.

19 [ The external space, created between the outer hydrogen permeable membrane tube (1) and the impermeable far outer shell (7), which receives the final permeate hydrogen, can be either empty, or may contain a selective catalyst (5) which converts permeate hydrogen after its combination with a component flowing in the external space parallel to the outer membrane tube. Such a flowing (sweep) component can be an unsaturated hydrocarbon (e.g., alkenes, alkynes) for conversion to saturated hydrocarbons after reaction with hydrogen, in an exothermic reaction. Flowing (sweep) component can be also carbon monoxide for direct production of methanol or gasoline (through Fischer-Tropsch synthesis) after combination with the permeate hydrogen in exothermic type reactions. Flowing gas can be nitrogen for exothermic ammonia synthesis after its combination with the permeate hydrogen. Other combination reactions of flowing species with permeate hydrogen can be these for reduction of aromatic hydrocarbons, also these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, these for reduction of alkyl and aryl halides and these for reduction of nitroalkanes and aromatic nitro compounds to corresponding primary amines.

The heat generated by exothermic reactions in the external shell, may be transferred into the catalytic reaction zone of the inner membrane tube via the radial direction, thus providing part of the heat load necessary to drive the endothermic catalytic reactions in the inner membrane tube. ]

19 The external space, created between the next inner membrane tube (1) and the impermeable far outer shell (7), which receives the final permeate hydrogen, can

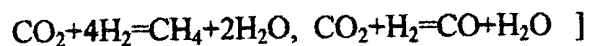
be either empty, or may contain a selective catalyst (5) which converts the permeate hydrogen after its combination with another component flowing via this external space. Such a flowing (sweep) component can be an unsaturated hydrocarbon (e.g., alkenes, alkynes) for conversion to saturated hydrocarbons after combination with hydrogen. Flowing (sweep) component can be also carbon monoxide for direct production of methanol or hydrocarbons (through Fischer-Tropsch synthesis) after combination with permeate hydrogen. Flowing gas can be nitrogen for exothermic ammonia synthesis after its combination with the permeate hydrogen. Other combination reactions of flowing compounds with permeate hydrogen can be these for reduction of aromatic hydrocarbons, also these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, these for reduction of alkyl and aryl halides and these for reduction of nitroalkanes and aromatic nitro compounds to corresponding primary amines.

20 Permeation of reaction products through the membrane tubes, especially hydrogen through the inner membrane tube, shifts the thermodynamic equilibrium conversion of reactant species to the product side and produces excess hydrogen and carbon oxide products within the catalytic reaction zone (4). Outer membrane tube thereby, serves as a final permeable medium for the recovery of highly pure hydrogen product for use in hydrogen utilization applications. Outer metal membrane tube serves also as a separation medium for hydrogen out of the central annular zone between the two membrane tubes, so that partial pressure of hydrogen lowers substantially along the annular zone, and therefore continuous driving force exists for hydrogen permeation from the catalytic reaction zone (4) to the central annular zone (8).

20 Permeation of reaction products through the membrane tubes, especially this of hydrogen through the most inner membrane tube (2), shifts the thermodynamic equilibrium conversion of reactant species into the product side and produces excess hydrogen and carbon oxides within the catalytic reaction zone (4). Next inner membrane tube (1) thereby, serves as a final permeable medium for the recovery of highly pure hydrogen product for use in hydrogen utilization applications. Membrane tube (1) serves also as a separation medium for hydrogen out of the central annular zone between the two membrane tubes, so that the partial pressure of hydrogen lowers substantially along the annular zone, and thereby continuous driving force exists for permeation of hydrogen from the catalytic reaction zone (4) into the central annular zone (8).

21 [ As an alternative to the invented design, for low operating gas reforming and dehydrogenation temperatures (e.g., between 200-400°C) in the absence of steam as a reactant, the inner membrane tube (2) can be made by porous inorganic or inorganic-metal materials and the outer membrane tube (1) can be made by organic materials which withstand high temperature (i.e., materials with high glass transition temperature,  $T_g$ ), and are permselective to both hydrogen and carbon dioxide which permeate through the inner tube (2) and flow along the central annular zone (8). The mixture of  $H_2$  and  $CO_2$  can be used directly in chemical synthesis applications such as this of alternative methanol synthesis via the reaction:  $CO_2 + 3H_2 = CH_3OH + H_2O$ , and as direct feed in molten carbonate fuel cells via the overall electrochemical reaction:  $H_2 + CO_2 + 1/2O_2 \rightarrow H_2O + CO_2$ . Moreover mixtures of  $H_2$  and  $CO_2$  can be converted to  $CH_4$  or  $CO$ , if a

special application requires, via the methanation or reverse water gas shift reactions respectively given below:



21 As an alternative to the invented process and design, for low operating gas reforming and dehydrogenation temperatures (e.g., between 200-500°C) and in the absence of steam as reactant, the most inner membrane tube (2) is made by inorganic or composite materials and the next inner membrane tube (1) is made by inorganic, composite, or high temperature polymer materials (i.e., materials with high glass transition temperature,  $T_g$ ) which are permselective to both hydrogen and carbon dioxide. The last two gases permeate through the next inner tube (1) as they flow along the central annular zone (8) after permeation from the most inner membrane (2). The recovered mixture of  $\text{H}_2$  and  $\text{CO}_2$  is used directly in chemical synthesis applications such as this of alternative methanol synthesis:  $\text{CO}_2 + 3\text{H}_2 = \text{CH}_3\text{OH} + \text{H}_2\text{O}$ , reaction (6), and as direct feed in molten carbonate fuel cells via the overall electrochemical reaction:



Moreover, recovered mixtures of  $\text{H}_2$  and  $\text{CO}_2$  are converted alternatively into  $\text{CH}_4$  or  $\text{CO}$  via the methanation or the reverse water gas shift reactions respectively as shown next:  $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$  (9),  $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$  (10),

22 The external (next inner) [(outer)] membrane (1) serves also as a backup membrane medium in case the most inner membrane (2) develops cracks or defects and its permselectivity to various gases increases. In this case, the next inner (outer) membrane (1) will selectively separate specific gases based on the selected membrane material as

described above. [Moreover, operational and maintenance service for replacing old or damaged membrane and outer non-membrane tubes becomes easier with the proposed design, because each part of the reactor is interconnected with the rest and can be disassembled and assembled accordingly.] Moreover, operational and maintenance service for replacing old or damaged membrane tubes and catalysts become easier with the proposed design, because the parts of the permreactor are interconnected properly via top and bottom caps and can be disassembled and assembled accordingly. The top and bottom ends where the tubes are interconnected are sealed with proper materials or welded or glazed to prevent gas flow or leak between the various compartments.

23 An optional design of the permreactor may include an additional catalytic zone (8) which is created between the most inner membrane tube (2) and the next inner membrane tube (1) and can be used in various reactions and processes. Heating of the reformer or reactor is achieved via cylindrical tubes (6) arranged symmetrically around the axial reactor axis and operated in the gas combustion regime by flowing waste type hydrocarbons or hydrocarbon-hydrogen mixtures mixed with oxygen or air. Unreacted hydrocarbons, carbon monoxide, non-permeate hydrogen or any mixture of these species from the catalytic reformer outlets (4), (5), (8), can be recycled as well into the heating [combustion] tubes (6). Flue or waste gases coming out from the interconnected fuel cells, engines or turbines can be also used directly to provide the necessary heat load into tubes (6). In an alternative heating configuration, a single tubular heating [cylindrical tube having the shape of a tube or a] coil is located along the reactor axis in zone (4) and can be operated by using same quality of combusted

gases. [In a third alternative configuration the symmetrically located tubes with flowing gas can be replaced by cylindrical electric heaters, heating bars or coils. ]

24 [Fig.2, shows multiple double permeable wall reactors of those described in Fig.1, but without the far outer impermeable tube (7), which are placed symmetrically inside a larger impermeable tube (A1), to create a multiple tube reformer with a common external area for collecting final permeate hydrogen.]

Fig.2, shows a lateral sectional view of the process permreactor described in Fig.1. The embodiment includes catalyst beds 4, 5 and 8 placed along the different tubular sections of the permreactor. The most inner tube bears inner membrane (2) while next inner tube bears outer membrane (1). The most inner tube includes tubular heating elements A6 along its axial length. Feedstock gases are entered into the permreactor via inlet ports A1 and the product and reactant gases exit via outlet ports A3. Alternative safety outlets A5 are located in the outer shell to discharge excess pressure in case of a sudden increase. Top and bottom caps A2 and A4 close the inlet and outlet of the tubular permreactor system and seal properly the ends of the different tubes by means of proper fittings or by using seal or glaze type materials or welding to prevent unwanted gas flow or leaks between the tubes.

25 [Fig.3 shows another developed reformer or reactor design to be used in steam and carbon dioxide reforming of hydrocarbons, steam reforming of alcohols, water gas shift and dehydrogenation reactions. Reformer or reactor consists of a most outer impermeable tubular cylinder (shell) (1) which is hollow inside in order to nest two more concentric tubular cylinders, a next inner one (2) and finally a most-inner (3) which both are made by permeable materials. Most outer cylinder (1) is made by impermeable

stainless steel or alloys, but next-inner cylinder (2) consists of metal, metal alloys, non-porous and porous inorganics, porous inorganic-metals or carbon materials such as those described in embodiment of Fig. 1.

The derived concentric cylindrical assembly has proper inlet and outlet fittings for feeding the feedstocks and discharging the post-reaction species. Proper inlet and outlet fittings are interconnected with the different sites of the cylindrical assembly. Fittings are connected to the annular space between most-outer and next-inner cylinders to deliver and collect gases flowing in this space. Additional independent fittings are connected to the annular space between the next-inner and most-inner cylinders to deliver and collect gases flowing in this space. Additional independent fittings are connected to the tubular space of the most-inner cylinder to deliver and collect gases flowing in this space. The fittings are made in such a manner so that they can seal in a leak-free manner each corresponding space, and the overall cross section of the double permeable wall cylindrical tube assembly. Before the fittings are applied and tighten, the annular space between the most outer (external) and next-inner cylinders is filled with the proper reaction catalyst in pellet or particle form to make the catalytic reaction zone (4). Proper catalyst is used for each reforming, water gas shift and dehydrogenation reactions. Catalysts used in these reactions are same with these mentioned above in description of embodiment of Fig. 1.

In steam,  $\text{CO}_2$  reforming of hydrocarbons, steam reforming of alcohols, water gas shift and paraffin dehydrogenation reactions, hydrogen is removed along the next-inner lateral cylindrical metal membrane surface (2), with carbon monoxide, carbon dioxide, steam, hydrocarbons, alcohols to possibly also permeate through inner lateral membrane

surface in a lesser degree than hydrogen depending on the membrane material used. An inert carrier gas such as argon, nitrogen, steam or a mixture of those gases, may flow along the permeate annulus, between tubes (2) and (3), through suitable inlet fittings, to carry the permeate components at a specific pressure value. Permeate hydrogen is further removed through permeation along the lateral surface of most-inner membrane tube (3) so that the final permeated stream contains pure hydrogen only, with pure hydrogen to be used in various applications including feed to synthesis reactors, gas turbines and engines, and fuel cells.

The most-inner membrane tube (3) is made by a metal, metal alloy, non-porous inorganic or carbon membrane which allows only hydrogen to permeate through and therefore purifies hydrogen from the permeating carbon oxides, steam and hydrocarbons, flowing in the annular zone created between the next-inner and most-inner cylindrical tubes. Membrane tubes (2) and (3) can be made with similar manufacturing techniques as those described in embodiment of Fig. 1. The most-inner membrane tube can be either empty or may contain a selective catalyst (5) which converts permeate hydrogen combined with another component flowing through the inner bore of this tube. Such a flowing (sweep) component can be an unsaturated hydrocarbon (e.g., alkenes, alkynes) for conversion to saturated hydrocarbons, after reaction with the permeate hydrogen in an exothermic reaction. Flowing (sweep) component for hydrogenation by the permeate hydrogen can be also carbon monoxide for direct production of methanol or gasoline hydrocarbons (through Fischer-Tropsch synthesis) in exothermic type reactions. Flowing (sweep) gas can be nitrogen for exothermic ammonia synthesis after combination with the permeate hydrogen. Other combination reactions with permeate hydrogen can be



these for reduction of aromatic hydrocarbons, also these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, these for reduction of alkyl and aryl halides and these for reduction of nitroalkanes and aromatic nitro compounds to corresponding primary amines. Alternatively, pure permeate hydrogen can be used as direct feed in hydrogen based turbines and engines, fuel cells, and other power generation equipment. The heat generated by exothermic reactions in the most-inner cylindrical bore, may be transferred into the catalytic reaction zone of the outer membrane cylinder via the radial direction, thus providing part of the heat load necessary to drive the endothermic catalytic reactions in catalyst bed (4) located within the outer membrane cylinder.

Permeation of hydrogen through the first inner membrane tube, shifts the thermodynamic equilibrium conversion of reactant species to the product side and produces excess hydrogen and carbon oxide products for reforming and water gas shift reactions, and hydrogen only for paraffin dehydrogenation reactions.

Most-inner membrane tube thereby, serves as a final permeable medium for the recovery of highly pure hydrogen product for use in hydrogen utilization applications. Most-inner metal membrane tube serves also as a separation medium for hydrogen out of the annular zone between the two hollow cylindrical membrane tubes, so that partial pressure of hydrogen lowers substantially along the annular zone, and therefore continuous driving force exists for hydrogen permeation from the enclosed catalytic reaction zone (4) to the central annular zone (7), through the next inner membrane tube (2).

As an alternative to the invented design, for low operating gas reforming and dehydrogenation reaction temperatures (e.g., between 200-400°C) and in the absence of

steam as a reactant, the next-inner membrane tube (2) can be made by porous inorganic or inorganic-metal materials which are permeable to several species diffusing out of the reaction zone (4), and the most-inner membrane tube (3) can be made by organic materials which withstand high temperatures (have high glass transition temperature,  $T_g$ ) and are permselective to both hydrogen and carbon dioxide species which flow along the central annular zone (7). The binary permeate mixture of  $H_2$  and  $CO_2$  can be used in applications described already in embodiment of Fig. 1.

The most-inner membrane serves also as a backup membrane medium in case the first-inner membrane develops cracks or defects and its permeability to various gases increases. In this case, the most-inner membrane will selectively separate specific gases based on the selected membrane material as described above. Moreover, operational and maintenance service for replacing old or damaged membrane and outer non-membrane tubes becomes easier with the proposed design, because each part of the reactor is interconnected with the rest and can be disassembled and assembled accordingly.

Heating of the described reformer or reactor is achieved via external heat provision (6). The external to the reformer combustion regime can be fueled by flowing waste type hydrocarbons or hydrocarbon-hydrogen mixtures mixed with oxygen or air. Unreacted hydrocarbons, carbon monoxide product, non-permeate hydrogen product, or any mixture of these post-reaction species coming out of the cylindrical reformer outlet connected with the catalyst zone (4), can be recycled as well into the external combustion-heating zone (6). Optionally, external heating of most-outer shell (1) can be provided by cylindrical type heaters or heating elements (i.e., made by ceramic, composite materials) in contact with the shell. ]

Fig.3, shows multiple double wall process permreactors of those described in Fig.1, after removal of the far outer impermeable tube (7), which all are placed symmetrically inside a larger impermeable tube (A1), to create a multiple tube reactor with a common external area for collecting final permeate hydrogen. The common external area may contain a catalyst (zone 5) wherein a catalytic reaction is conducted as described in Fig.1 above. This type of process configuration is able to process large amounts of reacting feedstocks and to produce larger throughputs of product mixtures in comparison with the single module process of Fig.1.

26 [Fig.4, shows multiple double permeable wall cylinder reactors of those described in Fig.3, which are placed symmetrically inside a larger impermeable tube (shell) (A1), to create a multiple tube reformer with a common external heating area. ]

26 Fig.4 shows the top cross sectional view of another developed double wall membrane process reactor (permreactor) used in the process of steam and carbon dioxide reforming of hydrocarbons, steam reforming of alcohols, water gas shift and alkane dehydrogenation reactions. Overall reactor process consists of a most outer hollow impermeable tube (outer shell) (1) which nests two more concentric hollow permeable tubes, a next inner one (2) and a most-inner (3). Most outer cylinder (1) is made by impermeable metal or alloy such as stainless steel. Next-inner membrane tube (2) is made by an inorganic or composite material which is permeable and selective to hydrogen and partly to the other reaction species.

27 The derived concentric multitube assembly has proper inlet and outlet fittings for feeding the feedstocks and discharging the post-reaction species similar to those described in Fig.1 and Fig.2 above. Inlet and outlet fittings are connected into

the ends of the three different tubular cylinders similarly to those shown in Fig.2, to deliver and collect gases flowing through these spaces. Top and bottom caps are also used to seal the ends of the overall reactor. Before the caps are applied and tighten, the annular space between the different cylinders is filled with the appropriate catalyst in pellet or particle form to make the catalytic reaction zones (4), (5) and (7). Proper catalyst is used for each reforming, water gas shift and dehydrogenation reactions. Catalysts used in these reactions are same with those mentioned above in the description of embodiment of Fig.1. The pressure is higher in zone (4) and drops progressively inwards from zone (4) to zone (7) to zone (5), with zone (5) to be at the lowest pressure. This pressure gradient assures the selective permeation and flow of gases inwards from membrane (2) to membrane (3).

28 In steam,  $\text{CO}_2$  reforming of hydrocarbons, steam reforming of alcohols, water gas shift and alkane dehydrogenation reactions, hydrogen is removed along the next-inner lateral membrane surface (2), with carbon monoxide, carbon dioxide, steam, hydrocarbons, alcohols to possibly also permeate through the same membrane surface in a lesser degree than hydrogen depending on the type of the membrane material used. An inert carrier gas such as argon, nitrogen, steam or a mixture of those gases, may flows along the permeate annular zone, between tubes (2) and (3), through the inlet fittings, to carry the permeate components at a specific pressure value. Permeate hydrogen is further removed through permeation along the lateral surface of most-inner membrane tube (3) so that final permeate stream contains pure hydrogen only, with pure hydrogen to be used in various subsequent

applications including feed to synthesis reactors, gas turbines and engines, and fuel cells.

29 The most-inner membrane tube (3) is made by a metal or non-porous inorganic membrane which allows only hydrogen to permeate through and therefore purifies the hydrogen from the permeating carbon oxides, steam, hydrocarbons and alcohols, flowing in the central annular zone (7). The membranes in tubes (2) and (3) are made with similar manufacturing techniques as those described in embodiment of Fig.1. Membranes (2) and (3) can act also as catalysts to partly catalyze the occurring reactions. The most-inner membrane tube can be either empty or may contain a selective catalyst (5) which can convert permeate hydrogen after combination with another component flowing through the inner bore of this tube. The reactions occurring are similar to these described in embodiment of Fig.1. Alternatively, pure permeated hydrogen can be used as direct feed in hydrogen based turbines and engines, fuel cells, and other power generation equipment.

30 Permeation of hydrogen through next inner membrane tube (2) shifts the thermodynamic equilibrium conversion of reactant species to the product side and produces excess hydrogen and carbon oxide products in zone (4). Most-inner membrane tube (3) thereby, serves as a final permeable medium for the recovery of highly pure hydrogen for use in hydrogen utilization applications. Most-inner membrane tube (3) serves also as a separation medium for hydrogen out of the central annular zone (7) so that partial pressure of hydrogen lowers substantially along the annular zone, and thereby continuous driving force exists for permeation of hydrogen from the catalytic reaction zone (4) into the central annular zone (7).

31 As an alternative to the disclosed process and design, for low operating gas reforming and dehydrogenation temperatures (e.g., between 200-500°C) and in the absence of steam as reactant, the next inner membrane tube (2) can be made by an inorganic or composite material and the most inner membrane tube (3) can be made by inorganic, composite, or high temperature polymer materials (i.e., materials with high glass transition temperature,  $T_g$ ) which are permselective to both hydrogen and carbon dioxide. The last two gases may first permeate through the inner membrane (2) and flow along the central annular zone (7) as they finally permeate through membrane tube (3). The recovered mixture of  $H_2$  and  $CO_2$  in zone (4) can be used in the applications already described in embodiment of Fig.1.

32 The most inner membrane tube (3) serves also as a backup membrane in case first inner membrane (2) develops cracks or defects and its permeability to various gases increases. In this case, the most inner membrane (3) will selectively separate specific gases including hydrogen, based on the selected membrane materials as described above. Operational and maintenance service for replacing old or damaged membrane tubes and catalysts in the described permreactor become easier with the proposed design, because the parts of the permreactor are interconnected properly via top and bottom caps and can be disassembled and assembled accordingly. The top and bottom ends of the interconnected tubes are sealed, glazed, or welded with proper materials to prevent gas flow and leaks between the various compartments.

33 An optional design of the permreactor may include an additional catalytic zone (7) which is created between the inner membrane tube (2) and the most inner membrane tube (3) and can be used in various reactions and processes.

34 Heating of the described reactor is achieved via external heat provision (zone 6). The external to the reformer combustion regime can be fueled by flowing waste type hydrocarbons or hydrocarbon-hydrogen mixtures mixed with oxygen or air. Flue or waste gases coming out from the interconnected fuel cells, engines or turbines can be also used directly to provide the necessary heat in zone (6). Unreacted hydrocarbons, carbon monoxide and non-permeate hydrogen products, or any mixture of these post-reaction species coming out of the outlets connected with the catalyst zones (4), (5) or (7) can be recycled as well into the external combustion-heating zone (6). Optionally, external heating of most-outer tube (1) can be provided by cylindrical type heaters or heating elements in contact with the outer tube. Thus, the lateral sectional view of the described processing permreactor in Fig.4 is similar with this of Fig.2 with the exception that there are no tubular type heaters in the most inner annular zone (5) as shown in Fig.1 and Fig.2.

35 [Fig.5 shows a cross section of a reformer or dehydrogenation reactor which consists of multiple cylindrical hollow polymer membrane tubes or fibers (1) nested within an outer impermeable metal cylindrical tube (2) which also contains the catalyst (3) in particle or pellet form, for the specific reactions mentioned below.

Reacting gas feedstocks free of steam such as  $\text{CO}_2$  and hydrocarbons also paraffin hydrocarbons are fed within the catalyst zone (3) through special inlet fittings and they react in the catalyst to produce hydrogen and carbon monoxide or hydrogen and olefins. Optionally, small volumetric quantities of hydrogen can be added into above feedstocks in inlet of the reactor assembly, to prevent heavy catalyst deactivation in the reactor inlet, wherein propensity for hydrocarbon cracking into carbon is high in absence of any

hydrogen. The CO<sub>2</sub> (dry) reforming or dehydrogenation catalysts are the same metallic type with those described in embodiment of Fig.1. Steam is avoided as a reactant in the reactor to avoid long term plasticization and structural damage of membrane tubes and loss of related permeability and selectivity properties.

Hydrogen product from these reactions is removed along the surface of the multiple membrane tubes (1), wherein the membranes are made by organic polymer or composite polymer membranes. Traces of carbon monoxide, carbon dioxide, product steam, olefins, and unreacted hydrocarbons may also permeate through the membrane tubes (1) in a lesser degree than hydrogen. The permeate gas mixture is continuously removed through the inner side of the membrane tubes and flows into a common impermeable metal shell which is interconnected with all the membrane tubes and sealed from the gases flowing into the catalytic reaction side (3). Optionally, a flowing component can flow along the inner membrane tube to sweep and dilute the permeate gas as it flows through the tubes.

In an optional design, catalyst in form of pellets or particles (4) can be contained within the inner side of the polymer membrane tubes to carry suitable catalytic reactions (such as hydrogenations) in which one of the reacting species is permeate hydrogen and the other reaction species are contained within the flowing gas. Such a flowing (sweep) component can be an unsaturated hydrocarbon (e.g., alkenes, alkynes) for conversion to saturated hydrocarbons, after reaction with hydrogen, in an exothermic reaction. Flowing (sweep) component can also be carbon monoxide for direct production of methanol or gasoline (through Fischer-Tropsch synthesis) after combination with the permeate hydrogen, in exothermic type reactions. Flowing gas can be nitrogen for exothermic



ammonia synthesis after its combination with the permeate hydrogen. Other combination reactions with permeate hydrogen over specific metallic catalysts, can be these for reduction of aromatic hydrocarbons, also these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, these for reduction of alkyl and aryl halides and these for reduction of nitroalkanes and aromatic nitro compounds to corresponding primary amines. Part of the heat generated by the exothermic reactions in the inner side of the tubes, may be transferred across the membranes, into the common catalytic reaction zone (3) surrounding the multiple membrane tubes, thus providing part of the heat load necessary to drive the endothermic catalytic reactions in catalyst zone (3).

Permeation of reaction products and especially hydrogen through the membrane tubes (1), shifts the thermodynamic equilibrium conversion of reactant species to the product side and produces excess hydrogen, carbon oxide, and olefins respectively within the catalytic reaction zone (3). Permeate collected hydrogen through the inner tubes (1), can be used in chemical synthesis or fuel applications as described in embodiment of Fig. 1.

As an alternative to the disclosed design, for low operating reforming and dehydrogenation temperatures (e.g., between 200-400°C), the inner tubes (1) can be made by materials which are permselective to both hydrogen and carbon dioxide products which permeate along the surface of the tubes (1). The separated mixture of H<sub>2</sub> and CO<sub>2</sub> can be used in applications described in embodiment of Fig. 1.

The main heating of the catalyst zone (3), is achieved via external heating (5) of the impermeable most-outer reactor shell (2) through combustion of flowing waste type hydrocarbons or hydrocarbon-hydrogen mixtures mixed with oxygen or air. Unreacted

hydrocarbons, carbon monoxide, non-permeate hydrogen or any mixture of these species coming out of the outlet of catalytic zone (3) can be recycled as well into the external combustion zone (5). Optionally, external heating of outer shell (2) can be provided by any type of cylindrical type heaters or heating elements (i.e., ceramic, composite).]

35 Fig.5, shows multiple double wall process permreactors of those described in Fig.4, which all are placed symmetrically, inside a larger impermeable tube (shell) (A1), to create a multiple tube permreactor with a common external heating area (6). The most outer impermeable tubes (1) which consist the external part of the multiple tubes are in direct contact with the common heating zone (6). This type of process configuration is able to process large amounts of reacting feedstocks and to produce larger throughputs of product mixtures in comparison with the single module process shown in Fig.4.

36 [Fig.6, depicts a system of catalytic permreactor with consecutive permeator (or optionally a permreactor) and optionally another final consecutive reactor, for conducting reforming and gas shift reactions. In Fig.6, stream 1 contains hydrocarbon feedstocks such as methane ( $\text{CH}_4$ ), higher alkanes (paraffins), naphtha, and natural gas, mixed with steam and  $\text{CO}_2$  and introduced in catalytic permreactor A for conducting simultaneously reactions (1), (2) and (3), or mixed with  $\text{CO}_2$  only for conducting reactions (2) and (3). Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation from hydrocarbon cracking especially in the inlet of permreactor A.

Catalytic permeable reformer A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with  $\text{H}_2$  to be separated in permeate stream 1b via valve A1,

in the general case.  $H_2$  and  $CO_2$  combined, can be separated in permeate stream in special applications, if an organic membrane is used in permreactor A. The rejected exit stream from the permreactor may contain product CO together with unreacted steam ( $H_2O(g)$ ),  $CO_2$ , and hydrocarbon, and non-permeate  $H_2$ . This stream becomes stream 2 and enters into heat exchanger B, where the unreacted steam is removed through condensation, and by the heat exchanging process new steam is generated in stream 6 from the water or steam of stream 5. Stream 6, can provide steam in permreactor A and reactor E through streams 9 and 10,18 respectively, in an alternative or simultaneous manner via use of valves B1,E1. The steam in 6 acquires the exchanged heat load from stream 2, the hot gas effluent of permeable reformer A, and thus its derived streams 9,10,18 can be mixed directly with streams 1 and 12 which are fed directly into reactors A and E respectively.

Steam from 6 is used via streams 10,18 and valves B1,E1 to provide the initial steam content in reformer E. Stream 7, passes through a bed of particles C (moisture adsorbent) to remove any non-condensed traces of moisture and through exit stream 8 enters into membrane permeator D. Stream 8, contains CO product, non-permeate  $H_2$  product, unreacted hydrocarbon (e.g.,  $CH_4$ ) and  $CO_2$  gases and has been cooled at the operating temperature of permeator D.  $H_2$  or both  $H_2$  and  $CO_2$  are removed in permeate stream 11 of permeator D, through the permselective action of a metal, non-porous inorganic, carbon, or organic membrane respectively. Non permeating stream containing hydrocarbon (e.g.,  $CH_4$ ), CO and  $CO_2$  or hydrocarbon and CO respectively, depending on the type of membrane used in permeator D, exits from permeator D, through stream 12 as reject stream. Stream 12 enters into reformer E, for conducting simultaneously reforming

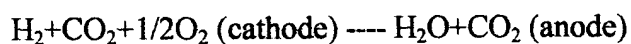
and water shift reactions selected from the group of reactions (1), (2) and (3), and be converted to final  $H_2$ , CO,  $CO_2$  or  $H_2$  and  $CO_2$  only products, depending on the feed composition of stream 12 in reformer E. Steam in reformer E is provided via stream 18. Unreacted steam is removed from exit stream 15 by passing this stream through heat exchanger F. Steam is generated from water or steam of stream 16 and via streams 17,18 and valve E1, the generated steam is fed into inlet of reformer E. Exit stream 19 contains  $H_2$ , CO,  $CO_2$  or  $H_2$ ,  $CO_2$  products and traces of unreacted hydrocarbons, depending on the operating conditions, that is the temperature, pressure, space velocity and feed composition of streams 12 and 18, of reformer E. Reformer E, can be replaced by a permeable reformer E similar to permeable reformer A, wherein  $H_2$  is separated in permeate and the reject exit stream 19 consists of CO and  $CO_2$  or  $CO_2$  only.

Reformers A and E are endothermic and flue gas streams 3,4 and 13,14 respectively are used to provide the necessary heat content to drive parallel reactions (1), (2) and (3) to completion. The two reformers can operate at same or different temperature and pressure conditions.

If conversion is high in permeable reformer A under certain operating conditions, the product in stream 2 is mainly CO and  $H_2$  which can be used directly as synthesis gas in methanol synthesis via the direct exothermic reaction:  $CO+2H_2=CH_3OH$ , also in Fischer-Tropsch type reactions for production of gasoline type hydrocarbons, and as fuel in gas turbines and engines and solid oxide fuel cells for power generation.

If the overall process consists of two reformers and the intermediate permeator, and the final product is a  $H_2$  and  $CO_2$  mixture in exit stream 19, it can be used separately or it can be mixed with stream 11 to make a combined  $H_2$  and  $CO_2$  stream. This

combined  $H_2$ ,  $CO_2$  mixture can be used for direct methanol synthesis via the exothermic reaction:  $3H_2+CO_2=CH_3OH(g)+H_2O(g)$ . Also, the  $H_2$ ,  $CO_2$  mixture can be used as direct feed in molten carbonate fuel cells for electricity generation via the overall electrochemical reaction:



Alternatively,  $CO_2$  can be condensed cryogenically from the binary mixture and pure hydrogen can be produced. Final  $H_2$  product can be used for chemical synthesis or as direct feed in fuel cells and gas turbines and engines for power generation applications (e.g., transportation, stationary). Applicable hydrogen driven fuel cells for utilizing the pure separated hydrogen from the process, include proton exchange membrane (PEM), solid oxide (SOFC), molten carbonate (MCFC), alkaline (AFC), phosphoric acid (PAFC) and modifications and combinations of these fuel cells.

Generated hydrogen product from the process can be combined with an unsaturated hydrocarbon (e.g., alkenes, alkynes) for conversion to saturated hydrocarbons in an exothermic type reaction. Also, with carbon monoxide for direct production of methanol (as described above) or gasoline (through Fischer-Tropsch synthesis) in exothermic type reactions. Hydrogen can be also combined with nitrogen for exothermic ammonia synthesis. Other combination (synthesis) reactions with permeate hydrogen can be these for reduction of aromatic hydrocarbons, also these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, these for reduction of alkyl and aryl halides and these for reduction of nitroalkanes and aromatic nitro compounds to corresponding primary amines.

The described process is able to overcome the thermodynamic equilibrium limitations of hydrocarbon ( $\text{CH}_4$ ) and  $\text{CO}_2$  reactant conversion, through the removal of  $\text{H}_2$  only, or of  $\text{H}_2$  and  $\text{CO}_2$  gases in membrane permreactor A and permeator D. The calorific value of the obtained  $\text{H}_2$ ,  $\text{CO}$  product in permreactor A, is higher than this of the reactant hydrocarbon (e.g.,  $\text{CH}_4$ ),  $\text{CO}_2$  and steam and the endothermic heat of reaction is stored in the products which can be subsequently used as fuels or in chemical synthesis.

Assuming 100% conversion of reactions (1) and (3) and reaction (2) in equilibrium in permreactor A, 2 mol of  $\text{CH}_4$  (with heat of combustion: 425.6 kcal), 1 mol of  $\text{CO}_2$  (with no heat of combustion), and 1 mol of  $\text{H}_2\text{O}(\text{g})$  (with no heat of combustion), produce 3 mol of  $\text{CO}$  (with heat of combustion: 202.8 kcal) and 5 mol of  $\text{H}_2$  (with heat of combustion: 341.5 kcal). These values are at  $25^\circ\text{C}$ . This corresponds to about 28% increase in calorific value for the product. Endothermic heat can be provided in reformers A and E through the combustion of flue or waste gases or unreacted recycled hydrocarbons coming out of the exit of reaction zone of reformers A and E as also described in Figs.1 and 3 above.

In an alternative design, permeator D is replaced by a catalytic permreactor D wherein the water gas shift reaction occurs if stream 8 is rich in product  $\text{CO}$ . In such case permreactor D is made by metal, non-porous inorganic, or carbon membranes to separate only hydrogen in permeate. Exit reject stream 12 from permreactor D contains product  $\text{CO}_2$  and unreacted steam and can be recycled in the first reforming permreactor or used in downstream applications either as a mixture or as pure  $\text{CO}_2$  after condensation of the steam. ]

36 Fig.6, depicts a process of catalytic permreactor with a consecutive permeator (or optionally with a second consecutive reactor) and with an optional third consecutive reactor, for conducting reforming and gas shift reactions. In Fig.6, stream 1 contains hydrocarbon feedstocks such as methane ( $\text{CH}_4$ ), higher alkanes (paraffins), naphtha, natural gas, mixed with steam and  $\text{CO}_2$  and introduced in catalytic permreactor A for conducting simultaneously reactions (1), (2) and (3), or mixed with  $\text{CO}_2$  only for conducting reactions (2) and (3). Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation from hydrocarbon cracking especially in the inlet of permreactor A.

37 Catalytic permreactor A can be any of the types of permreactors described in the embodiments of Fig.1, Fig.3, Fig.4, and Fig.5 above, with  $\text{H}_2$  in the general case to be separated in permeate stream 1b via valve A1.  $\text{H}_2$  and  $\text{CO}_2$  gases combined can be separated in permeate stream 1b in special applications, if a suitable organic, inorganic, or composite membrane is used in permreactor A. The rejected exit stream from the permreactor may contain CO product together with unreacted steam ( $\text{H}_2\text{O}(\text{g})$ ),  $\text{CO}_2$ , hydrocarbons, and non-permeate  $\text{H}_2$ . This stream becomes stream 2 and enters into a heat exchanger B, wherein the unreacted steam is removed through condensation and by the heat exchanging process new steam is generated in stream 6 from the water or steam of stream 5. Stream 6, can provide steam in permreactor A and reactor E through streams 9 and 10,18 respectively, in an alternative or continuous manner via use of valves B1 and E1. The steam in stream 6 acquires the exchanged heat load from stream 2, the hot gas effluent of

reformer A, and thus its derived streams 9,10,18 can be mixed directly with streams 1 and 12 which are fed directly into reactors A and E respectively.

38 Steam from stream 6 is used via streams 10,18 and valves B1,E1 to provide the initial steam content in reformer E. Stream 7, passes through a bed of particles C (a moisture adsorbent) to remove any non-condensed traces of moisture and through the exit stream 8 enters into membrane permeator D. Stream 8, contains CO product, non-permeate H<sub>2</sub> product, unreacted hydrocarbon (e.g., CH<sub>4</sub>) and CO<sub>2</sub> gases and has been cooled at the operating temperature of permeator D. H<sub>2</sub> or both H<sub>2</sub> and CO<sub>2</sub> are removed in permeate stream 11 of permeator D, through the permselective action of a metal, inorganic, polymeric or composite membrane respectively. Non permeating stream 12, containing hydrocarbons (e.g., CH<sub>4</sub>), CO and CO<sub>2</sub> or hydrocarbons and CO respectively, depending on the type of membrane used in permeator D, exits from permeator D, through stream 12 as reject stream. Stream 12 enters into reformer E, for conducting simultaneously reforming and water shift reactions selected from the group of reactions (1), (2) and (3), and be converted into final products H<sub>2</sub>, CO, CO<sub>2</sub> or H<sub>2</sub> and CO<sub>2</sub> only, depending on the feed composition of stream 12 in reformer E. Steam in reformer E is provided via stream 18. Unreacted steam is removed from exit stream 15 by passing this stream through a heat exchanger F. Steam is generated from water or steam of stream 16 and via streams 17,18 and valve E1, the generated steam is fed into the inlet of reformer E. Exit stream 19 contains H<sub>2</sub>, CO, CO<sub>2</sub> or H<sub>2</sub>, CO<sub>2</sub> products and traces of unreacted hydrocarbons, depending on the operating conditions, that is the



temperature, pressure, space velocity and feed composition of streams 12 and 18, of reformer E.

39 If conversion is high in permeable reformer A under certain operating conditions, the product in stream 2 is mainly CO and H<sub>2</sub> which can be used directly as synthesis gas for methanol and hydrocarbon synthesis, and as fuel in gas turbines, engines and solid oxide or molten carbonate fuel cells for power generation.

40 If the overall process consists of two reformers and the intermediate permeator, and the final product is a H<sub>2</sub> and CO<sub>2</sub> mixture in exit stream 19, it can be used separately or it can be mixed with stream 11 to make a combined H<sub>2</sub> and CO<sub>2</sub> stream. This combined H<sub>2</sub>, CO<sub>2</sub> mixture can be used for direct methanol synthesis via the exothermic reaction (6) or as direct feed in molten carbonate fuel cells for electricity generation. Alternatively, CO<sub>2</sub> can be condensed cryogenically from the binary mixture and pure hydrogen can be produced. Final H<sub>2</sub> product can be used for chemical synthesis or as direct feed in fuel cells and gas turbines and engines for power generation applications (e.g., transportation, stationary). Applicable hydrogen driven fuel cells for utilizing the pure separated hydrogen from the process, include proton exchange membrane (PEM), solid oxide (SOFC), molten carbonate (MCFC), alkaline (AFC), phosphoric acid (PAFC) and modifications and combinations of these fuel cells. Generated hydrogen product from streams 11b, 11, 19, can be combined with other chemical components in synthesis or combination type reactions as described above in Fig.1 and Fig.4.

41 The described process is able to overcome the thermodynamic equilibrium limitations of hydrocarbon (e.g., CH<sub>4</sub>) and carbon oxide (e.g., CO<sub>2</sub>) reactant

conversion, through the removal of  $H_2$  only, or of  $H_2$  and  $CO_2$  gases in permreactor A and permeator D. The calorific value of the obtained  $H_2$ , CO product in permreactor A, is higher than this of the reactant hydrocarbon (e.g.,  $CH_4$ ),  $CO_2$  and steam and the endothermic heat of reaction is stored in the products which can be subsequently used as fuels or in chemical synthesis.

42 Assuming 100% conversion of reactions (1) and (2) and reaction (3) in equilibrium in permreactor A, 2 mol of  $CH_4$  (with heat of combustion: 425.6 kcal), 1 mol of  $CO_2$  (with no heat of combustion), and 1 mol of  $H_2O(g)$  (with no heat of combustion), produce 3 mol of CO (with heat of combustion: 202.8 kcal) and 5 mol of  $H_2$  (with heat of combustion: 341.5 kcal). These values are at  $25^\circ C$ . This corresponds to about 28% increase in calorific value for the product. Endothermic heat can be provided in reformers A and E through flue or waste hot gases coming out of the interconnected fuel cells, turbines or engines and directed as input streams 3 and 13, as also described in Figs.1, 2, 3, 4, 5 above. Part of the exiting streams 2 and 15 can be also used to heat the reformers. The two reformers can operate at same or different temperature and pressure conditions.

43 In an alternative design, permeator D is replaced by a catalytic reforming reactor D wherein continuous conversion of the rejected reactants occurs from the previous step. In this case, vessels B and C are eliminated and the inlet stream 8 contains unreacted hydrocarbons, CO,  $CO_2$ , some  $H_2$  and unreacted steam. Additional steam can be added in stream 8 if necessary for the reforming reaction. The exit reject stream 12 from catalytic reactor D contains mainly products  $H_2$  and

CO after the unreacted steam condensation which can be used in similar applications as described above.

44 [Fig.7, describes a similar embodiment with the one described in Fig.6, but feed stream 1 contains carbon monoxide (CO) only, mixed with steam, and introduced in catalytic permreactor A which is filled with catalyst particles to conduct the water gas shift reaction only.

Catalytic permeable water gas shift reactor A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with  $H_2$  to be separated in permeate stream 1b via valve A1, in the general case.  $H_2$  and  $CO_2$  combined, can be separated in permeate stream for special applications, if an organic membrane is used in permreactor A. The rejected exit stream from the permreactor contains product CO together with unreacted steam ( $H_2O(g)$ ) and non-permeate  $H_2$ . This stream becomes stream 2 and enters into heat exchanger B, where the unreacted steam is removed through condensation, and by the heat exchanging process new steam is generated in stream 6 from the water or steam of stream 5. Stream 6, can provide steam in permreactor A and reactor E through streams 4 and 11,13 respectively, in an alternative or simultaneous manner via use of valves B1,F1. The steam in 6 acquires the exchanged heat load from stream 2, the hot gas effluent of permeable reactor A, and thus its derived streams 4,11,13 can be mixed directly with streams 1 and 12 which are fed directly into reactors A and E respectively.

Steam from 6 is used via streams 11,13 and valve F1 to provide initial steam in reactor E. Stream 7 passes through a bed of particles (moisture adsorbent) C to remove any non-condensed traces of moisture and through exit stream 8 enters into membrane permeator D. Stream 8 contains non-permeate product  $H_2$ , product  $CO_2$  and unreacted

CO gases and has been cooled at the temperature of permeator D.  $H_2$  and  $CO_2$  are removed in permeate stream 9 through permselective action of membrane in permeator D. Non permeating CO exits from permeator through stream 10 which can be called a reject stream. Stream 10 can be recycled via valve D1 and stream 3 into the first permeable shift reactor A for continuous shift reaction and conversion to  $H_2$  and  $CO_2$  products. Alternatively, by use of same valve D1, stream 10 becomes 12 which enters into reactor E for additional shift reaction (2), and conversion to final  $H_2$ ,  $CO_2$  products. Steam in E is provided via stream 13. Unreacted steam is removed from exit stream 14 by passing this stream through heat exchanger F. New steam is generated from water or steam of stream 15 and via streams 16,13 and valve F1 is fed into inlet of reactor E. Exit stream 17 contains  $H_2$ ,  $CO_2$  products and traces of unreacted CO depending on the operating conditions, that is the temperature, pressure and feed composition of streams 12 and 13, of reactor E.

Shift reactors A and E are exothermic and no heat input is necessary as with the previous endothermic reformers described in previous embodiments. Stream 1 needs to be preheated in temperature of permeable reactor A before entering into reactor. Using the heat content of streams 2 and 14 exiting from the reactors to provide the necessary heat content in the feed streams 4 and 13 entering into the reactors, the entire process operates in an autothermic way with no additional heat input necessary. The two shift reactors can operate at same or different temperature and pressure conditions.

Exit stream 17 can be used separately or it can be mixed with stream 9 to make a combined  $H_2$  and  $CO_2$  stream to be used for chemical synthesis or as fuel in applications similar to the ones mentioned above for the reforming reactors. Pure  $H_2$  from the process

can be recovered after the  $\text{CO}_2$  condensation and removal. Pure hydrogen from the process, can be used as fuel or in chemical synthesis applications, as described in embodiment of Fig.6 above.

The described shift process is able to overcome the equilibrium CO reactant conversion limitations, through removal of  $\text{H}_2$  in permreactor A and intermediate removal of  $\text{H}_2$  and  $\text{CO}_2$  products in permeator D. Thus, the process increases CO conversion and  $\text{H}_2$ ,  $\text{CO}_2$  yields above those obtained in conventional water gas shift reaction separation systems for production of  $\text{H}_2$  and  $\text{CO}_2$ . By use of the two heat exchangers each shift reactor operates in an autothermic way with no need of additional heat load in the system except for the initial preheating of stream 1 to start-up operation in permreactor A. ]

44 Fig.7, describes an embodiment of process similar to the one described in Fig.6, but the inlet stream 1 contains carbon monoxide (CO) only mixed with steam and introduced in catalytic permreactor A which is filled with catalyst particles to conduct the water gas shift reaction only.

45 Catalytic water gas shift permreactor A, can be any of the types of permreactors described in the embodiments of Fig.1, Fig.3, Fig.4, and Fig.5 above, with  $\text{H}_2$  in the general case to be separated in permeate stream 1b via valve A1.  $\text{H}_2$  and  $\text{CO}_2$  gases combined can be separated in permeate stream 1b for special applications, if an organic, inorganic, or composite membrane is used in permreactor A. The rejected exit stream from the permreactor contains product CO together with unreacted steam ( $\text{H}_2\text{O(g)}$ ) and non-permeate  $\text{H}_2$ . This becomes stream 2 and enters into a heat exchanger B, wherein the unreacted steam is removed through

condensation, and by the heat exchanging process new steam is generated in stream 6 from the water or steam of stream 5. Stream 6, can provide steam in permreactor A and reactor E through streams 4 and 11, 13 respectively, in an alternative or continuous manner via use of valves B1,F1. The steam in 6 acquires the exchanged heat load from stream 2, the hot gas effluent of permeable reactor A, and thus its derived streams 4,11,13 can be mixed directly with streams 1 and 12 which are fed directly into reactors A and E respectively.

46 Steam from stream 6 is used via streams 11,13 and valve F1 to provide initial steam in reactor E. Stream 7 passes through a bed of particles (a moisture adsorbent) C to remove any non-condensed traces of moisture and through exit stream 8 enters into membrane permeator D. Stream 8 contains non-permeate product  $H_2$ , product  $CO_2$  and unreacted CO gases and has been cooled at the temperature of permeator D.  $H_2$  and  $CO_2$  are removed in permeate stream 9 through permselective action of membrane in permeator D. Non permeating CO exits from permeator through stream 10 which can be called a reject stream. Stream 10 can be recycled via valve D1 as stream 3 into the first permeable shift reactor A for continuous shift reaction and conversion to  $H_2$  and  $CO_2$  products. Alternatively, by use of same valve D1, stream 10 becomes 12 which enters into reactor E for additional water gas shift reaction, and conversion into final  $H_2$ ,  $CO_2$  products. Unreacted steam is removed from exit stream 14 by passing this stream through heat exchanger F. New steam is generated from water or steam of stream 15 and via streams 16,13 and valve F1 is fed into inlet of reactor E. Exit stream 17 contains  $H_2$ ,  $CO_2$  products and traces of unreacted CO depending on the operating conditions,

that is the temperature, pressure, space velocity, and feed composition of streams 12 and 13 of reactor E.

47 Shift reactors A and E are exothermic and no heat input is necessary as with the previous endothermic reformers described in previous embodiments. Stream 1 needs to be preheated in temperature of permeable reactor A before entering into reactor. Using the heat content of streams 2 and 14 exiting from the reactors to provide the necessary heat content in the feed streams 4 and 13 entering into the reactors, the entire process operates in an autothermic way with no additional heat input necessary. The two shift reactors can operate at same or different temperature and pressure conditions.

48 Exit stream 17 can be used separately or it can be mixed with stream 9 to make a combined  $H_2$  and  $CO_2$  stream to be used for chemical synthesis or as fuel in applications similar to the ones mentioned in Fig.6. Pure  $H_2$  from the process can be recovered after the  $CO_2$  condensation and removal. Pure hydrogen from the process, can be used as fuel or in chemical synthesis applications, as described in embodiment of Fig.6 above.

49 The described shift process can overcome the equilibrium CO reactant conversion through removal of the  $H_2$  in permreactor A and the intermediate removal of  $H_2$  and  $CO_2$  products in permeator D. Thus, the process can increase the CO conversion and the  $H_2$ ,  $CO_2$  yields above the values obtained with conventional water gas shift reaction systems. By use of the two heat exchangers each shift reactor operates in an autothermic way with no need of additional heat load in the

system except for the initial preheating of stream 1 to start-up operation in permreactor A.

50 [ Fig.8 is an embodiment of a system of catalytic permreactor with consecutive permeator for conducting paraffin (alkane) dehydrogenation reactions. In Fig.8, stream 1 contains hydrocarbon feedstocks such as ethane, propane, n-butane, i-butane, naphtha, or liquid alkanes such as pentane, hexane, heptane. Liquid alkanes are vaporized by preheating before fed into catalytic permeable dehydrogenator A. Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation in the catalyst from hydrocarbon cracking especially in the inlet of permreactor A.

Catalytic permeable dehydrogenator A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with  $H_2$  to be separated in permeate stream 1b via valve A1. The rejected exit stream from permreactor A contains unreacted paraffins, product olefins, and non-permeate hydrogen. This stream becomes stream 2 and optionally passes through heat exchanger B, where by the heat exchanging process steam is generated in stream 6 from the water or steam of stream 5 to be used in steam requiring applications.

Stream 7, enters into membrane permeator C.  $H_2$  is removed in permeate stream 8 of permeator C, through the permselective action of a metal, non-porous inorganic, carbon or organic membrane. Non permeating stream containing hydrocarbons (product olefins and traces of unreacted paraffins) exits from permeator C, through stream 9 as reject stream. Stream 9 has composition dependent on the paraffin conversion in permreactor A and the hydrogen separation efficiency in permeator C. By optimizing



these two parameters, pure olefins can be produced in stream 9, to be used as direct feed in polyolefin reactors E for polyolefin production (i.e., polyethylene, polypropylene) exiting from stream 10. Olefins from stream 9 are also used as direct feed in synthesis reactors, such as ethylene for ethylene oxide and ethylene glycol production, propylene for propylene oxide and propylene glycol production, isobutylene for oxygenated gasoline production. Produced pure hydrogen from the described process can be used into same fuel and synthesis applications as described in embodiment of Figs. 1 and 3.

Paraffin dehydrogenation reactions are endothermic, and reactor A receives heat from flue gas streams 3,4 to drive dehydrogenation reactions (4) to completion.

The described process is able to overcome the thermodynamic equilibrium limitations of paraffin hydrocarbon conversion met in conventional reactors, through the removal of product  $H_2$  in membrane permreactor A and permeator C. Endothermic heat can be provided in dehydrogenator A through the combustion of flue or waste hydrocarbons or unreacted recycled hydrocarbons from the reaction zone of reactor A as also described in embodiments of Figs. 1,3 and 5 above.

Permeable dehydrogenator A can be substituted by non-permeable (e.g., non-porous stainless steel wall) dehydrogenator A. Valve A1 and stream 1b are eliminated and all post-reaction gases exit from stream 2. Permeator C still operates in same function as described above. ]

50 Fig.8 is an embodiment of a process of a catalytic dehydrogenation permreactor for conducting alkane (paraffin) dehydrogenation reactions, followed by a consecutive olefin synthesis reactor. In Fig.8, stream 1 contains hydrocarbon feedstocks such as ethane, propane, n-butane, i-butane, naphtha, or liquid alkanes

such as pentane, hexane, heptane. Liquid alkanes are vaporized by preheating before fed into the catalytic membrane dehydrogenator A. Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation in the catalyst from hydrocarbon cracking especially in the inlet of permreactor A.

51 Catalytic permeable dehydrogenator A, can be any of the types described in embodiments of Figs.1, 3, 4, 5 above, with  $H_2$  to be separated in permeate stream 1b via valve A1. The rejected exit stream from permreactor A contains unreacted paraffins, product olefins, and traces of non-permeate hydrogen and unreacted paraffins. This becomes stream 2 and optionally passes through a heat exchanger B to lower its temperature, wherein by the heat exchanging process steam is generated in stream 6 from the water or steam of stream 5 to be used in steam requiring applications.

52 Stream 7, enters into reactor C which can be an olefin to polyolefin polymerization reactor or a specialty chemicals production reactor from olefins. Polyolefins produced in reactor C in stream 8 can be polyethylene from ethylene monomer which is coming from ethane dehydrogenation in permreactor A. Also, polypropylene from propylene monomer which is coming from propane dehydrogenation in permreactor A. Similarly, higher polyolefins can be produced from dehydrogenation of higher paraffins. Specialty chemicals production in reactor C include ethylene oxide, ethylene glycol, acetaldehyde, acrolein and acrylic acid from ethylene. Also, propylene oxide, propylene glycol and acrylonitrile from propylene, and methyl tert-butyl ether (MTBE) from isobutylene.

The produced pure hydrogen from the described process in stream 1b, can be used within the same fuel utilization and synthesis applications as described in embodiments of Fig.1 and Fig.4. Paraffin dehydrogenation reactions are endothermic, and permreactor A receives heat from flue gas streams 3 and 4 to drive the dehydrogenation reactions (4) to completion.

53 The described process is able to overcome thermodynamic equilibrium limitations for paraffin conversion met in conventional reactors, through the removal of  $H_2$  product in membrane permreactor A. Endothermic heat can be provided in dehydrogenator A through the combustion of flue or waste hydrocarbons or unreacted recycled hydrocarbons from the reaction zone of reactor A; also from flue hot gas heated by the heat of the exothermic reactions taking place in synthesis reactor C, as also described in embodiments of Fig.1 and Fig.4 above.

54 [ Fig.9, is an embodiment which is related with these described in Figs.6 and 7, but with stream 1 to contain hydrocarbon feedstocks such as methane or higher alkanes such as naphtha and natural gas, also alcohol feedstocks such as methanol, ethanol, propanol, butanol mixed with steam only and introduced in catalytic permreactor A which is filled with catalyst particles to conduct the methane steam reforming reaction (1) and the simultaneously occurring water gas shift reaction (2). Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation from hydrocarbon cracking especially in the inlet of the reactor A.

Catalytic permeable reformer A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with  $H_2$  to be separated in permeate stream 1b via valve A1, in the general case.  $H_2$  and  $CO_2$  combined, can be separated in permeate stream in

special applications, if an organic membrane is used in permreactor A. The rejected exit stream from the permreactor may contain product  $\text{CO}_2$ ,  $\text{CO}$ , unreacted steam ( $\text{H}_2\text{O}(\text{g})$ ) and hydrocarbon, and non-permeate  $\text{H}_2$ . This stream becomes stream 2 and enters into heat exchanger B, where the unreacted steam is removed through condensation, and by the heat exchanging process new steam is generated in stream 8 from the water or steam of stream 7. Stream 8, can provide steam in permreactor A and reactor E through streams 6 and 10,20 respectively, in an alternative or simultaneous manner via use of valves B1,E1. The steam in 8 acquires the exchanged heat load from stream 2, the hot gas effluent from permeable reformer A, and thus its derived streams 6,10,20 can be mixed directly with streams 1 and 14 which are fed directly into reactors A and E respectively.

Steam from 8 is used via streams 10,20 and valve E1 to provide initial steam in reformer E. Stream 9 passes through a bed of particles (moisture adsorbent) C to remove any non-condensed traces of moisture and through exit stream 11 enters into membrane permeator D. Stream 11 has been cooled in temperature of permeator D and contains  $\text{CO}$ ,  $\text{CO}_2$ , unreacted hydrocarbon, non-permeate  $\text{H}_2$  gas species.

$\text{H}_2$  or both  $\text{H}_2$  and  $\text{CO}_2$  are removed in permeate stream 12 of permeator D, through the permselective action of a metal, non-porous inorganic, carbon or organic membrane respectively. Non permeating stream containing hydrocarbon (e.g.,  $\text{CH}_4$ ),  $\text{CO}$  and  $\text{CO}_2$  or hydrocarbon and  $\text{CO}$  respectively, depending on the type of membrane used in permeator D, exits from permeator D, through stream 13 as reject stream. In case wherein stream 13 contains hydrocarbon and  $\text{CO}$  it can be recycled via valve D1 and stream 5 into first permeable reformer A for continuous reforming and conversion to main  $\text{H}_2$  and  $\text{CO}_2$  products. Alternatively, by use of valve D1, stream 13 becomes stream

14 which enters into steam reformer E for additional reforming and shift reactions, via reactions (1) and (2) and additional conversion to  $H_2$  and  $CO_2$  products. In case wherein stream 13 contains hydrocarbon, CO and  $CO_2$ , using valve D1, stream 13 becomes stream 14 which enters into modified steam and  $CO_2$  reformer E for additional reforming and shift reactions, via reactions (1), (2) and (3) and conversion to  $H_2$ , CO,  $CO_2$  products. Reformer E, can be replaced by a permeable reformer E similar to permeable reformer A, wherein  $H_2$  is separated in permeate and the reject exit stream 17 consists of product CO and  $CO_2$  or  $CO_2$  only.

Reformers A and E are endothermic and flue gas streams 3,4 and 15,16 respectively are used to provide the necessary heat content to drive parallel reactions (1), (2) and (3) to completion. The two reformers can operate at same or different reaction temperature and pressure conditions.

If conversion is high in permeable steam reformer A under certain operating conditions, the product in stream 2 is mainly  $CO_2$  and non-permeate  $H_2$  which can be used directly in applications described already in embodiment of Figs. 1 and 3.

If the overall process consists of two reformers and the intermediate permeator, and the final product is  $H_2$  and  $CO_2$  in exit stream 21, this product can be used separately or it can be mixed with stream 12 to make a combined  $H_2$  and  $CO_2$  stream to be used in similar applications.

Alternatively,  $CO_2$  can be condensed cryogenically from the binary mixture and pure hydrogen product is produced. Final  $H_2$  product can be used for chemical synthesis or as direct feed in fuel cells and gas turbines and engines for power generation

applications (e.g., transportation, stationary), same to these described in embodiment of Fig.6.

The described process is able to overcome the thermodynamic equilibrium limitations of hydrocarbon ( $\text{CH}_4$ ) and steam reactant conversion, through the removal of  $\text{H}_2$  product only, or of the combined  $\text{H}_2$  and  $\text{CO}_2$  products in membrane permreactor A and permeator D. The calorific value of the obtained  $\text{H}_2$ ,  $\text{CO}_2$  product in permreactor A, is higher than this of the reactant hydrocarbon (e.g.,  $\text{CH}_4$ ) and steam mixture, because the provided endothermic heat of reaction is stored in the products and can be subsequently released by using products as fuels or in chemical synthesis.

Assuming 100% conversion of reactions (1) and (2), 1 mol of  $\text{CH}_4$  (with heat of combustion: 212.8 kcal) and 2 mol of  $\text{H}_2\text{O}(\text{g})$  (with no heat of combustion) generate 1 mol of  $\text{CO}_2$  (with no heat of combustion) and 4 mol of  $\text{H}_2$  (with heat of combustion: 273.3 kcal). These values are at  $25^\circ\text{C}$ . This corresponds to about 28% increase in calorific value for the product gases. By providing external heat through flue or waste gas input in the reformers and with the described two heat exchangers in place, the energy requirement of the one reactor-one permeator or two reactor-one permeator cascades is fulfilled and the processes operates in a thermally independent manner providing for an energy efficient design. Endothermic heat can be provided in reformers A and E through the combustion of flue or waste gases or unreacted recycled hydrocarbons from the reaction zone of reformers A and E, as also described in Figs.1,3,5 above. ]

**54** Fig.9, is a process embodiment which is related with those described in Figs.6 and 7, but with stream 1 to contain hydrocarbon feedstocks such as methane or higher alkanes such as naphtha and natural gas, also alcohol feedstocks such as

methanol, ethanol, propanol, butanol mixed with steam only and introduced in catalytic permreactor A which is filled with catalyst particles to conduct the methane steam reforming reaction (1) and the simultaneously occurring water gas shift reaction (3). Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation from hydrocarbon cracking especially in the inlet of permreactor A.

55 Catalytic permreactor A, can be any of the permreactor types described in embodiments of Figs.1,3,4,5 above, with  $H_2$  to be separated in permeate stream 1b via valve A1, in the general case.  $H_2$  and  $CO_2$  combined, can be separated in permeate stream 1b in special applications, if an organic, inorganic, or composite membrane is used in permreactor A. The rejected exit stream from the permreactor may contain product  $CO_2$ ,  $CO$ , unreacted steam ( $H_2O(g)$ ), hydrocarbons, alcohols, and non-permeate  $H_2$ . This becomes stream 2 and enters into heat exchanger B, wherein the unreacted steam is removed through condensation, and by the heat exchanging process new steam is generated in stream 8 from the water or steam of stream 7. Stream 8, can provide steam in permreactor A and reactor E through streams 6 and 10,20 respectively, in an alternative or continuous manner via use of valves B1,E1. The steam in 8 acquires the exchanged heat load from stream 2, the hot gas effluent from permeable reformer A, and thus its derived streams 6,10,20 can be mixed directly with streams 1 and 14 which are fed directly into reactors A and E respectively. Steam from stream 8 is used via streams 10,20 and valve E1 to provide the initial steam in reformer E. Stream 9 passes through a bed of particles (a moisture adsorbent) C to remove any non-condensed traces of moisture and through

exit stream 11 enters into membrane permeator D. Stream 11 has been cooled in temperature of permeator D and contains CO, CO<sub>2</sub>, unreacted hydrocarbons, and non-permeate H<sub>2</sub> gas species.

56 H<sub>2</sub> or both H<sub>2</sub> and CO<sub>2</sub> are removed via permeate stream 12 of permeator D, through the permselective action of a metal, inorganic, polymer or composite membrane. Non permeating stream 13 containing hydrocarbons (e.g., CH<sub>4</sub>), alcohols, CO and CO<sub>2</sub> or hydrocarbons, alcohols, and CO respectively, depending on the type of the membrane used in permeator D, exits from permeator D, through the reject stream 13. In case wherein stream 13 contains hydrocarbons, alcohols, and carbon monoxide (CO) it can be recycled via valve D1 and stream 5 into first permeable reformer A for continuous reforming and conversion to main H<sub>2</sub> and CO<sub>2</sub> products. Alternatively, by use of valve D1, stream 13 becomes stream 14 which enters into steam reformer E for additional reforming and shift reactions, (reactions (1), (3)), and conversion to H<sub>2</sub> and CO<sub>2</sub> products. In case wherein stream 13 contains hydrocarbons, CO and CO<sub>2</sub>, by use of valve D1, stream 13 becomes stream 14 which enters into modified steam and CO<sub>2</sub> reformer E for additional reforming and shift reactions, via reactions (1), (2) and (3) and conversion into H<sub>2</sub> and CO products.

57 Reformers A and E are endothermic and flue gas streams 3,4 and 15,16 respectively are used to provide the necessary heat content to drive parallel reactions (1), (2) and (3) to completion. The two reformers can operate at same or different reaction temperature and pressure conditions. If conversion is high in permeable reformer A under certain operating conditions, the product in stream 2 is



mainly  $\text{CO}_2$  and non-permeate  $\text{H}_2$  which can be used directly in  $\text{H}_2$ ,  $\text{CO}_2$  applications described already in embodiment of Figs. 1 and 4.

58 If the overall process includes a second conventional reformer E and the intermediate permeator as shown in Fig.9, and the final product is  $\text{H}_2$  and  $\text{CO}_2$  in exit stream 21, this product can be used separately or it can be mixed with stream 12 to make a combined  $\text{H}_2$  and  $\text{CO}_2$  stream to be used in similar applications. Alternatively,  $\text{CO}_2$  can be condensed cryogenically from the binary mixture and pure hydrogen product can be produced. Final  $\text{H}_2$  product can be used for chemical synthesis or as direct feed in fuel cells, gas turbines and engines for power generation applications (e.g., transportation, and stationary), same to those described in embodiments of the previous figures. The waste flue gas streams coming out of the interconnected fuel cells or engines and turbines, are used as streams 3 and 15 to heat the reformers A and E.

59 By providing external heat through flue or waste gas combustion in the reformers or through internal stream recycling and with the described two heat exchangers in place, the energy requirement of the one reactor-one permeator or two reactor-one permeator cascades is fulfilled and these processes operate in a thermally independent manner providing for an energy efficient design. Endothermic heat can be provided also in reformers A and E via the combustion of exit or recycled streams from the reaction zone of reformers A and E (streams 2, 17), as also described in Figs.1,2,3,4,5 above.

60 [ Fig.10, is an embodiment of a steam and CO<sub>2</sub> hydrocarbon reforming process which includes a permeable reformer or a non-permeable reformer followed by a cryogenic separator for separation of certain post-reaction gases exiting from the reject exit of the reformer. In Fig.10, stream 1 is introduced into catalytic permreactor A, containing hydrocarbon feedstocks such as methane (CH<sub>4</sub>) mixed with steam and CO<sub>2</sub> for conducting simultaneously reactions (1), (2) and (3), or mixed with CO<sub>2</sub> only for conducting reactions (2) and (3). Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation from methane cracking especially in the inlet of permreactor A.

Catalytic permeable reformer A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with H<sub>2</sub> to be separated from the reformer, and exit in permeate stream 1b via valve A1. The rejected exit stream from the permreactor contains product CO together with unreacted steam (H<sub>2</sub>O(g)), CO<sub>2</sub>, and hydrocarbon, and non-permeate H<sub>2</sub>. This stream becomes stream 2 and enters into a steam condenser C wherein the unreacted steam is condensed and by the heat exchanging process new steam is generated in stream 17 from the water or steam of stream 16. Steam through stream 17 is recycled into stream 1 in inlet of reformer A. Stream 5 free of steam, exits from condenser C and enters into cryogenic separator B, which operates at a temperature lower than the boiling temperature of carbon dioxide and hydrocarbons so that these compounds are separated as liquids and collected in the bottom of the separator (operating cryogenic temperature of the separator is a negative number which has larger absolute value than the absolute value of any of the boiling points of the liquified components above). However, operating cryogenic temperature of separator is higher

than the boiling points of carbon monoxide and hydrogen so that these compounds remain in the gas phase and exit from the separator as a gas mixture (operating cryogenic temperature of the separator is a negative number which has smaller absolute value than the absolute value of the boiling points of both hydrogen and carbon monoxide). Liquified components exit via stream 7 through valve B1. Gas phase hydrogen and carbon monoxide exit as stream 6 via valve B2. Liquified stream 7 can be recycled into the feed stream of reformer A (stream 1) via stream 8 after evaporation in evaporator D. Alternatively, stream 8 can be further processed in another reforming reactor by becoming stream 9 which enters into reformer E, for additional steam and CO<sub>2</sub> reforming of any remaining hydrocarbons via reactions (1), (2) and (3). Optional, steam in reformer E is provided via stream 18. Stream 10 exiting the reformer can optionally condense the containing unreacted steam by passing through the heat exchanger F. Inlet stream 11 contains water which becomes steam in stream 12 after passing through F. Steam in stream 12 can optionally fed into reformer E via valve E1. Stream 13 exiting the heat exchanger F is dry, and contains H<sub>2</sub> and CO as main products with traces of unreacted hydrocarbons and CO<sub>2</sub> depending on the operating temperature and pressure of the reformer E and the composition of feed streams 10 and 12.

Recovered H<sub>2</sub> and CO in stream 13 can be either used separately or optionally be combined with stream 6 from the separator to make one stream to be used as fuel or in chemical synthesis. Direct application of the produced H<sub>2</sub> and CO mixture is in methanol synthesis via the direct exothermic reaction:  $\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$ , also in Fischer-Tropsch type reactions for production of gasoline type hydrocarbons, and as fuel in gas turbines and engines and solid oxide fuel cells for power generation. Similarly, H<sub>2</sub> recovered in

stream 5, can be used as fuel or in chemical synthesis, as described in embodiment of Fig.6. The described process is able to overcome the thermodynamic equilibrium limitations of hydrocarbon (e.g.,  $\text{CH}_4$ ), steam and  $\text{CO}_2$  reactant conversion, through the removal of  $\text{H}_2$  and  $\text{H}_2$  and  $\text{CO}$  gases in membrane permreactor A and cryogenic separator B respectively. Endothermic heat in reformers A and E is provided through gas streams B respectively. Endothermic heat in reformers A and E is provided through gas streams 3,4 and 14,15 respectively. Streams 3, 14 can be fed by a bypass stream of exit stream 2, as also described in embodiments of Figs.1,3,5. The reformer A can be optionally substituted by a non-permeable reformer A, wherein stream 1b and valve A1 are eliminated and all product  $\text{H}_2$  is included in post-reaction mixture entering through stream 2 into cryogenic separator B. ]

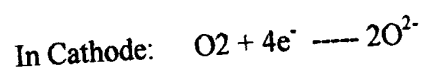
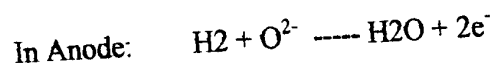
60 Fig.10, is a new embodiment of a steam and  $\text{CO}_2$  hydrocarbon reforming process which includes a permeable reformer or a non-permeable reformer followed by a cryogenic separator for separation of certain post-reaction gases exiting from the reject exit of the reformer. In Fig.10, stream 1 is introduced into catalytic permreactor A, containing hydrocarbon feedstocks such as methane ( $\text{CH}_4$ ) mixed with steam and  $\text{CO}_2$  for conducting simultaneously reactions (1), (2) and (3), or mixed with  $\text{CO}_2$  only for conducting reactions (1) and (2). Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation from methane cracking especially in the inlet of permreactor A.

61 Catalytic permeable reformer A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with  $\text{H}_2$  to be separated from the reformer, and exit in permeate stream 1b via valve A1. The rejected exit stream from the permreactor contains product  $\text{CO}$  together with unreacted steam ( $\text{H}_2\text{O(g)}$ ),

$\text{CO}_2$ , and hydrocarbon, and non-permeate  $\text{H}_2$ . This becomes stream 2 and enters into a steam condenser C wherein the unreacted steam is condensed and by the heat exchanging process new steam is generated in stream 17 from the water or steam of stream 16. Steam through stream 17 is recycled into stream 1 in inlet of reformer A. Stream 5 free of steam, exits from condenser C and enters into cryogenic separator B, which operates at a temperature lower than the boiling temperature of carbon dioxide and hydrocarbons so that these compounds are separated easily as liquids and collected in the bottom of the separator. However, the operating cryogenic temperature of separator is higher than the boiling points of carbon monoxide and hydrogen so that these compounds remain in gas phase and exit from the separator as a gas mixture. Liquified components exit via stream 7 through valve B1. Gas phase hydrogen and carbon monoxide exit as stream 6 via valve B2. Liquified stream 7 can be recycled into the feed stream of reformer A (stream 1) via stream 8 after evaporation in evaporator D. Alternatively, stream 7 can be further processed in another reforming reactor by becoming stream 9 which enters into reformer E, for additional steam and  $\text{CO}_2$  reforming of any remaining hydrocarbons via reactions (1), (2) and (3). Optionally, steam in reformer E is provided via stream 18 which is a bypass stream of stream 17. Stream 10 exiting the reformer can optionally condense the containing unreacted steam by passing through the heat exchanger F. Steam in stream 12 can optionally fed into reformer E via valve E1. Stream 13 exiting the heat exchanger F is dry, and contains  $\text{H}_2$  and CO as main products with traces of unreacted hydrocarbons and  $\text{CO}_2$  depending on the operating temperature and pressure of the reformer E and the composition of feed streams 9 and 12.

62 Recovered  $H_2$  and CO in stream 13 can be either used separately or optionally be combined with stream 6 from the separator to make one stream to be used as fuel in conventional and fuel cell systems or in chemical synthesis. Direct application of the produced  $H_2$  and CO mixture is in methanol synthesis via the reaction (5), also in Fischer-Tropsch reactions for production of gasoline range hydrocarbons, as fuel in gas turbines and engines, and in solid oxide and molten carbonate fuel cells for power generation. Similarly,  $H_2$  recovered in stream 1b, can be used as fuel or in chemical synthesis, as described in previous embodiments.

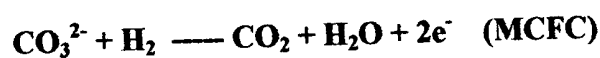
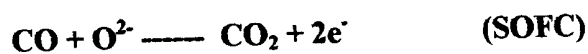
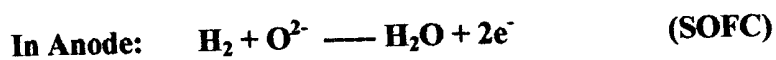
63 [Fig.11, is a modified embodiment of the process described in Fig.6. It applies to complete conversion of hydrocarbon (i.e.,  $CH_4$ ) and  $CO_2$  reactants of stream 1, within the permeable reformer A, to  $H_2$  and CO products. The occurring reactions are (1),(2),(3) or (2),(3) only. Catalytic permeable reformer A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with  $H_2$  to be separated in permeate stream 3 via valve A1. Exiting from the permreactor, stream 2, containing only CO and non-permeating  $H_2$ , or CO, non-permeating  $H_2$ , and traces of unreacted steam, enters into a solid oxide fuel cell (SOFC) unit B. Stream 2 is directed in the anode of the solid oxide cell, and consists the fuel constituent of the fuel cell.  $O_2$  in stream 4, is directed in the cathode of the fuel cell and consist the oxidant, for the well known electrochemical reaction conducted within the cell with electric current generation:

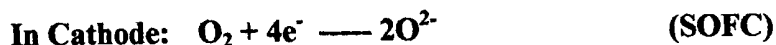
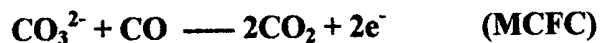


Optionally, part of hydrogen from permeate stream 3, can be fed into stream 2, via bypass stream 3b, to adjust the composition of  $H_2$  in stream 2 to that required to feed the

fuel cell B. The reformer A can be optionally substituted by a non-permeable reformer A, wherein all product H<sub>2</sub> is included in exit stream 2. Flue gas streams 5 and 6, are used to provide the endothermic heat content into the reformer A. Stream 5 can be fed by a bypass stream of exit stream 2, as also described in embodiments of Figs.1,3,5. Permeable reformer A can be substituted by a non-permeable (e.g., stainless steel) reformer A. Valve A1 and stream 3, 3b are eliminated and all post-reaction gases exit from stream 2. Fuel cell B still operates in same function as described above.]

63 Fig.11, is a modified embodiment of the process described in Fig.6. It applies to a complete conversion of hydrocarbons (e.g., CH<sub>4</sub>), CO<sub>2</sub>, and steam reactants of stream 1, within the permeable reformer A, to H<sub>2</sub> and CO products. The occurring reactions are (1),(2), (3) or (2),(3) only. Catalytic permreactor A, can be any of the types described in embodiments of Figs. 1,3,4 and 5 above, with H<sub>2</sub> to be separated in permeate stream 3 via valve A1. The exiting from the permreactor, stream 2, containing only CO and non-permeating H<sub>2</sub>, or CO, non-permeating H<sub>2</sub>, and traces of unreacted steam, enters into a solid oxide (SOFC) or molten carbonate (MCFC) fuel cell which is unit B. Stream 2 is directed in the anode of the fuel cell, and makes the fuel constituent of the fuel cell. Stream 4 consists of O<sub>2</sub> or air for SOFCs, and of CO<sub>2</sub>-O<sub>2</sub>, or CO<sub>2</sub>-air mixtures for MCFCs respectively, and is directed in the cathode of the fuel cell B. Stream 4 is therefore the oxidant, for the known electrochemical reactions conducted within the two cells for electric current generation:





64      Optionally, part of hydrogen from permeate stream 3, can be fed into stream 2, via bypass stream 3b, to adjust the composition of  $\text{H}_2$  in stream 2 to that required to feed the fuel cell B. Flue gas stream 5 is used to provide the endothermic heat content into the reformer A. Stream 5 can be fed by a bypass stream of exit stream 2, as also described in embodiments of Figs.1,3,4,5. Moreover, stream 7 which is the flue hot gas from the fuel cell, can be also directed into stream 5 to make the hot heating gas in reformer A. Reformer A can be optionally substituted by a non-permeable reformer A, wherein all catalytically produced  $\text{H}_2$  is contained into the exit stream 2. Valve A1 and streams 3 and 3b are eliminated and all post-reaction gases exit from stream 2. Fuel cell B still operates in same function as described above with flue gas stream 7 from the fuel cell to heat the reformer A.

65      [ Fig.12, is an embodiment which describes a modified operation of the process described in Fig.6. It applies to complete conversion of hydrocarbon (i.e.,  $\text{CH}_4$ ) and  $\text{CO}_2$  reactants of stream 1, within the permeable reformer A, to  $\text{H}_2$  and CO products. The occurring reactions within the reformer are (1),(2),(3) or (2),(3) only. Catalytic permeable reformer A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with  $\text{H}_2$  to be separated in permeate stream 1b via valve A1. Exiting from the permreactor, stream 2, containing only CO and non-permeating  $\text{H}_2$ , or CO, non-permeating  $\text{H}_2$ , and traces of unreacted steam, passes through heat exchanger B and moisture adsorbent C to remove unreacted steam, and enters into permeator D as a dry



stream. Hydrogen is separated in stream 11 from carbon monoxide, rejected by the membrane, and exiting via stream 12. Carbon monoxide, via stream 12, can be optionally fed into a consecutive water gas shift reactor E for conversion to final  $H_2$  and  $CO_2$  products. A heat exchanger F is used in exit of the water gas shift reactor E, to remove any unreacted steam, with final stream 15 to contain only  $H_2$  and  $CO_2$ . The reformer A can be optionally substituted by a non-permeable reformer A, wherein all reaction product  $H_2$  is included in exit stream 2 and stream 1b, valve A1 are eliminated.

Hydrogen from stream 11 can be used in applications mentioned already in embodiment described in Fig.6 and Fig.9. Similarly CO from stream 12, or  $H_2$  and  $CO_2$  from stream 15 can be used in aforementioned applications described already in embodiments of Figs.6,9 and 10. ]

65 Fig.12, is a modified embodiment of the process described in Fig.6. It pertains to methanol production from the products of the reforming reaction occurring in permeactor A, and the subsequent utilization of methanol in a methanol fuel cell. The process describes the complete conversion of hydrocarbons (e.g.,  $CH_4$ ),  $CO_2$  and steam reactants, in stream 1, within the permeable reformer A, into  $H_2$  and CO products. The occurring reactions are (1),(2),(3) or (2),(3) only. Catalytic permeable reformer A, can be any of the types described in embodiments of Figs. 1,3,4, and 5 above, with  $H_2$  to be separated in permeate stream 1b via valve A1. The exiting from the permeactor, stream 2, containing CO, non-permeating  $H_2$ , and some unreacted  $CO_2$ , or CO, non-permeating  $H_2$ ,  $CO_2$  and traces of unreacted steam, passes through heat exchanger B and moisture adsorbent C to remove unreacted steam and result in an all dry stream of  $H_2$ , CO and  $CO_2$ . Stream 8, of  $H_2$  and CO products (synthesis

gas) enters into the methanol synthesis reactor D, wherein methanol is produced via the following exothermic reactions:  $\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$ , and  $\text{CO}_2 + 3\text{H}_2 = \text{CH}_3\text{OH} + \text{H}_2\text{O}$

66 Reactor D, can be a slurry or catalytic plug flow reactor with methanol to be produced in gas or liquid phase depending on the temperature, pressure and feed composition into the reactor and the type of catalyst used. Zinc, copper and chromium oxide catalysts are well known to convert synthesis gas to methanol. Methanol from stream 9 can be fed into a methanol driven fuel cell for electricity generation or for further use as a synthesis chemical including the synthesis of higher hydrocarbons.

67 Optionally, stream 1c, which is a bypass stream of stream 1b and contains pure hydrogen, can be recycled into stream 8 via stream 16 to adjust hydrogen composition in this stream where necessary, and to increase the efficiency of methanol synthesis in reactor D. Product hydrogen from stream 1b can be used in fuel, fuel cell, and synthesis applications. Reformer A is endothermic and flue gas streams 3,4 are used to provide the necessary heat content to drive parallel reactions (1), (2), (3) to completion. The waste or flue gas stream from the interconnected methanol fuel cell and the exothermic methanol reactor D, can be used to provide the heat content in stream 3 to heat the reformer A. Stream 3 can be also fed by a bypass stream of stream 2 if necessary. In an alternative process modification, reactor D can be replaced by a catalytic reactor to conduct Fischer Tropsch reactions for production of olefin range hydrocarbons from the  $\text{H}_2$  and  $\text{CO}$  feed or from the  $\text{H}_2$ ,  $\text{CO}$  and  $\text{CO}_2$  feed.

68 [ Fig.13, is an embodiment of a modified process of the process described in Fig.6. It pertains to methanol production from the products of the reforming reaction occurring in reactor A, and the subsequent utilization of methanol in a methanol-steam reforming reactor. The process describes the complete conversion of hydrocarbon (i.e.,  $\text{CH}_4$ ) and  $\text{CO}_2$  reactants, in stream 1, within the permeable reformer A, to  $\text{H}_2$  and  $\text{CO}$  products. The occurring reactions are (1),(2),(3) or (2),(3) only. Catalytic permeable reformer A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with  $\text{H}_2$  to be separated in permeate stream 1b via valve A1. Exiting from the permreactor, stream 2, containing only  $\text{CO}$  and non-permeating  $\text{H}_2$ , or  $\text{CO}$ , non-permeating  $\text{H}_2$ , and traces of unreacted steam, passes through heat exchanger B and moisture adsorbent C to remove unreacted steam and yield an all dry stream of  $\text{H}_2$  and  $\text{CO}$ . Stream 8, of  $\text{H}_2$  and  $\text{CO}$  (synthesis gas) enters into the methanol synthesis reactor D, wherein methanol is produced via the following exothermic reaction:  $\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$ ,  $\Delta H^\circ_{298} = -128.2 \text{ kJ/mol}$  (13.1). Reactor D, is a three phase slurry type reactor or a catalytic plug flow reactor with methanol to be produced in gas or liquid phase depending on the temperature, pressure and feed composition in the reactor and the type of catalyst used. Zinc, copper and chromium oxide catalysts are well known to convert synthesis gas to methanol. Methanol from stream 9 is fed to a methanol driven fuel cell for electric current generation. Optionally, stream 9 containing methanol enters into steam reforming reactor E for continuous catalytic methanol-steam reforming reaction in similar type catalysts. The reforming reaction in reactor E is as follows:  $\text{CH}_3\text{OH} + \text{H}_2\text{O} = 3\text{H}_2 + \text{CO}_2$ ,  $\Delta H^\circ_{298} = 49.5 \text{ kJ/mol}$  (13.2). Exiting from the reactor E, gaseous stream 11, condenses unreacted steam and methanol in heat exchanger F, and the exit product gas through

stream 14 is  $H_2$  and  $CO_2$ . Steam in reactor E is provided through streams 6,10,13,20 which is generated by the heat exchanging process in heat exchangers B and F.

Pure  $H_2$  and  $CO_2$  mixture from exit stream 14, can be used as feed in molten carbonate fuel cells or in alternative methanol synthesis via the opposite reaction of methanol steam reforming, listed above. Optionally, bypass streams 15, 16 can be fed into stream 8 to add  $CO_2$  and  $H_2$  into the synthesis gas mixture fed into reactor D, to adjust its composition for increasing methanol production efficiency in the catalyst in reactor D via the reverse (13.2) reaction. Optionally also, stream 1c, which is a bypass stream of stream 1b and contains pure hydrogen, can be recycled into stream 8 via stream 16, for adjusting the hydrogen composition in this stream where necessary, to increase the efficiency of methanol synthesis in reactor D. Streams 15 and 1c merge into stream 16 via valve D1.

Hydrogen in stream 14 can be used as a mixture with  $CO_2$ , or as pure  $H_2$  after the  $CO_2$  condensation and removal.

Produced hydrogen from streams 1b and 14, can be used in applications mentioned already in embodiments described in Fig.6 and Fig.9. The  $H_2$  and  $CO_2$  mixture of stream 14 can be used in synthesis or fuel applications mentioned already in same embodiments. Reformers A and E are endothermic and flue gas streams 3,4 and 18,19 respectively are used to provide the necessary heat content to drive parallel reactions (1), (2), (3) and (13.2) respectively to completion. Streams 3 and 18 can be fed by a bypass stream of stream 2. Optionally, reformer A can be a non-permeable reformer with only one post-reaction outlet (exit), this of stream 2, which delivers all products and unreacted reactants into the heat exchanger B and next into reactor D. ]

### [Abstract of the Disclosure]

[Overall permreactor-separator process designs and effective permreactor designs with increased mass and heat transfer, reactant conversion, product yield and optional recycling for processing methane, hydrocarbons, alcohols, carbon monoxide, natural gas, acidic natural gas, coal gas, biomass gas, and mixtures of hydrocarbons with carbon dioxide, based on the reforming reactions of these feedstocks with steam and carbon dioxide and the dehydrogenation reactions of saturated hydrocarbons. Final exit streams from these gas phase processors contain pure hydrogen, hydrogen and carbon monoxide mixture, hydrogen and carbon dioxide mixture, and can be used as a direct feed in molten carbonate, solid oxide, proton exchange membrane, alkaline, phosphoric acid and other types of hydrogen driven fuel cells. Same final exit processed streams can be alternatively used for direct chemical synthesis such as methanol, for hydrogenations and hydrogen based reduction reactions such as those of unsaturated hydrocarbons to paraffins, and as feed in power generation systems such as gas turbines and gas engines.]

### ABSTRACT OF THE DISCLOSURE

Multiwall (e.g., double wall) permreactor and permreactor-separator processes by integrating reaction and separation operations in one reactor with increased reactant conversion and synthesis gas yield and internal stream recycling, by defining more than one catalytic zones, and by employing more than one membranes made by different materials, for the catalytic in-situ processing and

conversion of methane, higher hydrocarbons, alcohols, carbon monoxide, natural gas, coal- landfill- and biomass gases, and other flue and waste mixtures of methane and higher hydrocarbons, based on the reforming reactions of these feedstocks with steam and carbon dioxide, as well as on dehydrogenation reactions of alkane hydrocarbons. Final exit streams from the described gas phase processing reactors and systems, contain pure hydrogen or synthesis gas (hydrogen and carbon monoxide, hydrogen and carbon dioxide mixtures), and can be used as direct feed in molten carbonate, solid oxide, proton exchange membrane, alkaline, phosphoric acid and related types of hydrogen driven fuel cells as well as in gas turbines and engines. Same exit gas streams can be alternatively used for direct chemical synthesis in a variety of reactions including methanol and fuel hydrocarbon synthesis, hydrogenation, hydrocracking, and hydrogen based reduction and synthesis reactions.